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THE INSTITUTE OF PETROLEUM

SYMPOSIUM ON INSULATING OILS

SECOND SESSION

At the opening of the evening session the Chairman, **P. W. L. Gossling,** made the following remarks: The papers considered so far have mainly been studies of the mechanism of catalysed oxidation, leading possibly to improvements in testing methods with regard to the accuracy of their prediction of the behaviour of oils in service, and with regard to their precision.

On the other hand, a better knowledge of the effects of hydrocarbon composition upon oxidation stability, resulting from these fundamental studies, may make it easier to cope with the increasing demands of transformer engineers. The electrical industry is stated to be expecting to apply as a feature of normal practice short periods of overload to transformers during their daily load cycles. It is understood that an attempt is to be made, by instituting a BS Code of Practice, to rationalize the loading by reference to temperatures rather than to electrical loading. However, the effect of high temperatures upon the life of the cellulosic insulation imposes limitations and although peak temperatures for oil may become higher, it is suggested that the temperatures in the remainder of the operating cycle may be such that no very serious overall increase in the severity of the conditions for the oil occurs. This is stated in a questioning manner, and it would be very interesting to hear the views of electrical engineers in the course of our discussion.

Where conditions do become more onerous, as for generator transformers, with their fairly uniform high loading for long periods, and for certain transformers in industry, the use of anti-oxidants may come into its own. We have this evening three papers dealing with this from various aspects.

J. C. Wood-Mallock, H. Steiner, and L. G. Wood deal with catalyst inactivation. The dissolution of copper in oil is shown to occur to varying extents with oils of varying types. This is not prevented by the introduction of copper complexing agents, rather is it increased, while oxidation inhibitors of secondary amino or phenolic type appear to be neutral. Combinations of certain of the two types of compound are, however, shown to be effective and, in the case of anthranilic acid as complexing agent, there is evidence of the formation of a surface film. The authors suggest that the secondary amine has an anti-oxidant effect upon the adsorbed layer. In oxidation tests it is shown that, among the complexing agents used, only ethylenediamine and anthranilic acid have any oxidation retarding effect, but combinations of either of these, or of certain allied compounds, with oxidation inhibitors have anti-oxidant effects considerably greater than are attributable to the separate compounds. This paper opens up for discussion a useful alternative approach to anti-oxidation, and further developments should be possible.

In the paper of J. H. T. Brook there is further evidence in support of existing views that the mechanism of inhibitor action is the scavenging of peroxide radicles by the inhibitor. With a series of oils from various sources the chain initiation rate for the decomposition of added di-*tert*-butyl peroxide is used as a measure of the reactivity of the hydrogen atoms in the oils, and this is shown to correlate with their induction periods in oxygen absorption tests with soluble copper catalyst. This provides an indirect method for the determination of the inhibitor susceptibility of oils.

The usefulness of oxygen absorption tests as a research tool is shown already in three papers at this meeting, and its potential practical value is emphasized in that of L. Massey and A. C. M. Wilson. The authors have first reported, with a thoroughness that is highly to be commended, an investigation of the effects of variations of test conditions. The method is then used to study a number of considerations important in the practical use of inhibited oils. The conclusions which are drawn satisfactorily reflect the results of the experimental work.

On the question of the mechanism of inhibited oxidation, the observation that the induction periods of oils are independent of, or change only slightly with, catalyst concentration is possibly worthy of further discussion in its relation to formula (1) of Brook's paper.

With certain types of oil the authors find the concept of the useful life period more informative than that of induction period. The useful life period also has the possibility of measurement with simpler apparatus and with greater precision.

In its consideration of inhibited oils, ERA has felt it advisable first to limit itself to the organization and supervision of field trials in order to find out how inhibited oil behaves in service, and what criteria of deterioration are the most useful. The Association accepts the fact that the development of laboratory tests for the initial assessment of new inhibited oils should be undertaken in due course. These papers and their discussion tonight may well lead more quickly to a beginning of such work. We shall be especially interested to hear whether our European colleagues have yet any experiences to tell us as, to judge from discussions at CIGRE meetings over the last few years, there has so far been in Europe a considerable reluctance to embark very generally upon the use of inhibited oils.

The final paper of our series is upon an entirely different aspect. G. E. Bennett tells us about the assessment of the properties of insulating oils by electrical tests. This paper will be found of great value for an up-to-date summary of the main factors involving the properties of insulating oils as assessed by electrical measurements, and is of special interest at this juncture, as IEC has recently embarked upon collaborative studies of electric strength measurement. Regarded as tests for water, the relative advantages of this measurement and those for loss angle and resistivity, the several alternatives of which are summarized, are worthy of discussion.

A A

THE EFFECT OF METALS ON TRANSFORMER OILS AND SOME METHODS OF PROTECTION AGAINST ADVERSE EFFECT*

By J. C. WOOD-MALLOCK† (Fellow), H. STEINER† (Fellow), and L. G. WOOD†

SUMMARY

The copper content of fifty-six samples of transformer oil from small distribution transformers was found to range from 0·2 to 0·6 p.p.m., with a few samples having contents up to 6 p.p.m. The solubility of copper in a number of transformer oils prepared from different crudes and/or by different methods was studied. The effect of chelating agents, and combination of chelating agents and oxidation inhibitors on the solubility of copper in these oils and on their oxidation characteristics was investigated. The behaviour of the best of these combinations of chelating agents and oxidation inhibitors was compared in a number of oils and in several of the accelerated tests with that of oxidation inhibitors when used in these oils alone.

INTRODUCTION

EXAMINATION of transformer oils from operating units has shown that small amounts of copper are usually present in solution.[1-3] Copper in this form is a powerful accelerator of oxidation, and hence of acidity and sludge formation. There is also evidence that this effect is not confined to the soluble state but that it can be produced by the solid metal also,[4] although this latter point is not universally accepted. Experimental evidence to compare the effect of solid and soluble copper on a quantitative basis has hitherto been lacking, but is now available.[5] It appears from these results that soluble copper is the much more powerful catalyst.

Of the other metals likely to be contacted by transformer oils, iron has been found in solution in these oils and is active in promoting oxidation, though to a lesser degree than copper.[6] Solid iron also accelerates oxidation, but the effect is not very marked unless specially prepared metal surfaces are used.[1]

At present the most general method of combating the oxidation of oils, including specifically metal-catalysed oxidation, is by the action of anti-oxidants, which either substantially retard or completely suppress oxidation for a limited time, the induction period, after which oxidation may proceed at the rate characteristic of the uninhibited oil. There is considerable evidence that this type of inhibition is due to an interaction of the inhibitor with the radicals produced in the decomposition of peroxides formed as primary oxidation products, thus inhibiting the propagation of the chain reaction involved in the oxidation process.[7, 8] This type of inhibition of oxidation has been used for a considerable time in a variety of petroleum products, including insulating and transformer oils.

It now seems likely that the step in the oxidation reaction which is catalysed by heavy metals is that of initiation, generally associated with generation of free radicals through the decomposition of peroxides or hydroperoxides.[9] The propagation and termination reactions are influenced by metals to only a minor extent. The latter reactions are still susceptible to inhibition by the same anti-oxidants which are effective in the absence of metal catalysts, and this is the reason for their successful application in the case of metal-catalysed oxidations.

In the case of metal catalysis, however, a different type of inhibition is possible through deactivation or passivation of the metal itself. In this case, inhibition would not be due to suppression of the chain propagation reaction, but of the heavy-metal catalysed initiation reaction.[10-13] Thus there is the possibility that the different molecular mechanism which is operative in this type of inhibition may give rise to new effects which may be of value in practice.

It is well-known that complexes of metals and of metal salts often show properties which differ from those of the uncomplexed metal or metal ion. The reactivity of the metal can be decreased or enhanced, depending both on the particular metal and the complexing agent. In the case of copper, the catalytic activity is as a rule diminished or altogether suppressed; in the case of iron both increases and decreases of the catalytic power have been observed.[12, 13]

Complexing is particularly effective if it is done by compounds which form metal chelates, and an application of this type has been used in the petroleum industry for some years. In order to minimize deterioration of cracked gasoline which has been sweetened by oxidative treatment employing a copper salt, disalicylal-ethylenediamine or disalicylal-propylenediamine is added. These compounds effectively suppress the formation of gum-like polymers which would otherwise result from oxidation of the gasoline,

* MS received 17 December 1957.

† Manchester Oil Refinery Ltd.

accelerated in this case by the soluble copper present as a residue of the sweetening process. These salicylaldehyde derivatives form very stable chelates with the copper, the catalytic activity of which then becomes negligible.[10]

In the case of transformer oil, although the problem is similar the operating conditions are not. In the first place, the temperatures at which the chelating agents must be effective are higher (ambient temperature in the case of the gasoline storage application and 60°–100° C for transformer oil). Equally, the temperatures at which the usual acceptance tests are performed are higher. A temperature of 100° C is used in the accelerated gum test for gasoline, whereas temperatures from 100° to 150° C, depending on the particular test method used, are usual in transformer oil testing. These higher temperatures are in the region where most chelating agents are unstable, particularly under oxidizing conditions. Instability at the temperatures of the accelerated tests would indicate a similar instability at operating temperatures over the very long periods of service which are expected of transformer oils. A further point is that, in the case of the electrical oil application, the inhibitor not only has to interact effectively with soluble copper compounds but must preferably protect bare and insulated copper surfaces.

In one respect, the anti-oxidant action is easier in the case of insulating oils. In the gasoline application, the anti-oxidant has to protect very easily attacked olefins, whereas in transformer oils olefins are absent and the compounds most easily attacked are alkyl aromatics, which are considerably more resistant to oxidation than olefins.

Stoker and Thompson [14] have introduced a useful general classification of anti-oxidants.

(1) *Catalyst Passivators*

Compounds which form a chemically combined, or physically adsorbed film on the catalyst surface.

(2) *Catalyst Deactivators*

Compounds which render oil-soluble metallic compounds catalytically inactive by converting them to compounds or complexes in which the metallic ion is prevented from exercising its catalytic influence, prevention being by precipitation of the metal or by the prevention of electron transfer processes.

(3) *Oxidation Inhibitors*

Compounds, usually of the amino or phenolic type, which react with the oxidation chain carriers, converting them to inactive products and breaking the reaction sequence.

(4) *Indirect Anti-oxidants*

Compounds which become active, in any of the above ways, only after oxidation has commenced.

This paper is concerned primarily with anti-oxidants of types (1) and (2), but although the distinction between these two classes is logical, it is difficult to maintain in practice because it is found, as will be shown later, that compounds which are effective deactivators (Group (2)) can also be effective catalyst passivators (Group (1)).

In the later parts of the paper it will also be necessary to distinguish between oils inhibited by oxidation inhibitors (type (3)) and oils containing anti-oxidants of type (1) and/or (2) with or without the addition of inhibitors of type (3). For the sake of simplicity we shall refer to the first type of oil as inhibited, and the second type as passivated oils.

In this paper are first presented some data on the soluble copper content of used transformer oils. The authors have also studied the rate of dissolution of metallic copper in transformer oil and the influence of oxidation inhibitors, deactivators, and passivators. Finally, the development of effective additives for use in transformer oils based on a combination of the above anti-oxidants is described, and the behaviour of these passivated oils under various accelerated conditions of testing is compared with that of inhibited oils.

SOLUBILITY OF COPPER IN TRANSFORMER OILS

The authors have determined the copper content of over fifty samples of transformer oil, taken from a random selection of small distribution transformers, *i.e.* those working under conditions of service where oxidation effects are most pronounced.

The oil samples as received were in all cases clear, with no visible sludge. They were filtered before analysis.

Copper concentrations were determined by the method of Buchwald and Wood,[15] using an ion-exchange technique, or by the acid washing method described below.

> 50 g of oil, diluted with an equal volume of 60°–80° C petroleum ether, were washed with six 10-ml portions of 28 per cent v/v sulphuric acid and one 10-ml portion of de-ionized water. The combined acid washings were wet-ashed, using nitric acid followed by 100 vol hydrogen peroxide as necessary, and the copper content determined by the sodium diethyl dithiocarbamate method.

The results are given in Table I, and it will be seen that soluble copper compounds were present in all samples tested.

Most of the oils had copper contents between 0·2 and 0·6 p.p.m., but in some cases much higher values were found. Acidities were between 0·02 and 17·4 mg KOH/g. No correlation between soluble copper content and acid value could be established. Fig 1 shows the distribution of copper content over the samples examined.

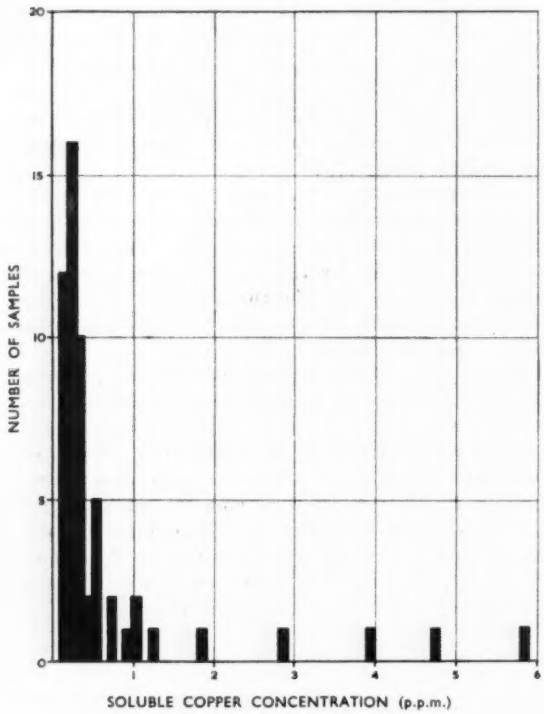

FIG 1

DISSOLVED COPPER IN USED TRANSFORMER OIL

It being clear that all oils in service were capable of taking copper into solution, it appeared important to learn whether oils varied in their ability to dissolve metallic copper. The following test method was devised for this purpose:

> 200 ml of the oil under test was placed in a 400-ml beaker in contact with a strip of 0·1-mm thick electrolytic copper foil, 25 cm × 4 cm, cleaned by the method prescribed in IP 56. Beakers were immersed in a bath at 70° ± 0·1° C and the test oil stirred gently with a glass propeller-type agitator. A "Perspex" cover held slightly above the upper rim of the beaker prevented contamination by dust, while providing access of air to the oil. Experiments were carried out in duplicate, and at the end of a suitable period (normally 72 hours) the acid value, peroxide number, and soluble copper content of the oil were determined.

Base Oils

The above method was used to test a number of transformer oils, in particular one batch of oil refined to B.S. 148 : 1951 specification (Oil A), while some work was also carried out on a batch of oil refined to B.S. 148 : 1951 specification from the same crude but by a different method (Oil B). A further oil (Oil C) was a technical white oil prepared from the same crude as Oils A and B.

Oils D, E, F, and G were samples of commercial transformer oils prepared from different crudes.*

The physical and chemical characteristics of the oils were determined by standard methods. The oils were also analysed for hydrocarbon groups by the *n–d–M* method,[16] and by a chromatographic separation on silica gel.[17]

TABLE I

Soluble Copper Content and Acidity of Oils from Transformers in Service

Copper content, p.p.m.	Acidity, mg KOH/g	Copper content, p.p.m.	Acidity, mg KOH/g
0·11	0·20	0·32	0·13
0·12	0·04	0·33	0·04
0·12	0·24	0·33	0·45
0·14	0·01	0·33	0·49
0·15	0·03	0·34	0·36
0·15	0·07	0·35	0·02
0·15	0·29	0·36	0·07
0·16	0·09	0·36	0·34
0·17	0·23	0·36	0·54
0·18	0·02	0·38	0·22
0·18	0·99	0·40	17·4
0·19	0·07	0·49	0·07
0·20	0·04	0·50	0·11
0·20	0·19	0·55	0·29
0·21	0·31	0·55	0·69
0·22	0·16	0·59	0·22
0·22	0·16	0·60	0·31
0·22	0·18	0·70	0·02
0·25	0·10	0·74	0·07
0·25	0·13	0·90	0·20
0·25	0·17	1·00	0·14
0·26	0·31	1·04	0·49
0·26	1·80	1·28	2·18
0·27	0·31	1·80	0·11
0·28	0·04	2·80	0·23
0·28	0·04	3·90	8·90
0·28	0·45	4·70	2·34
0·28	0·47	5·80	0·32

The results of these analyses are reported in Table II.

Examination of Table II shows that the various oils differed, particularly in their aromatic content. Oil A had twice the aromatic content of Oil B, while Oil C, a highly refined oil, contained only 1·4 per cent of aromatics. This was further confirmed by the structural group analysis. It is seen that aromatic ring structures are absent from Oil C (within the limits of this method of analysis) and that in Oil B their concentration is much smaller than in Oil A.

Oil D is rather similar to Oil B, but has a somewhat smaller proportion of aromatic compounds, while Oil E is less paraffinic in structure than any of the other oils and is high in aromatic content. Oil F contains the same percentage of aromatics as Oil B, but is more paraffinic. Oil G is similar to Oil A. All oils, except Oil F, which has an appreciable content of

* Oils F and G mentioned in Table II were not used in the solubility experiments but in further work mentioned later in the text.

sulphur (0·47 per cent), contain less than 0·05 per cent sulphur.

Additives Studied

One of the main objects of this work was to determine the effect of a variety of additives on the solubility of copper in transformer oil. Of the additives used the following were commercial products:

Phenyl-β-naphthylamine (PBN)
2,6-Di-tertiary-butyl-4-methyl-phenol (DBPC)
2,4-Dimethyl-6-tertiary-butyl-phenol (24M6B)
Disalicylal-ethylenediamine ("Nonoxol CD," ex ICI Ltd.)
Disalicylal-propylenediamine ("Tenamene 60," ex Tennessee Eastman Corporation)

All other additives were laboratory reagents of the highest purity available.

TABLE II

Physical and Chemical Characteristics of the Oils

Property	Oil A	Oil B	Oil C	Oil D	Oil E	Oil F	Oil G
Density at 20° C	0·8822	0·8694	0·8529	0·8698	0·8846	0·8616	0·8790
Flash point (P.M. closed) ° F	300	305	305	310	305	305	305
Pour point ° F	below −60	below −65	below −30	below −60	below −40	below −50	below −60
Acid value, mg KOH/g	0·03	0·03	nil	nil	nil	0·03	0·03
Viscosity cS at 70° F	24·4	23·4	24·7	31·3	29·4	19·2	24·3
Refractive index at 20° C	1·4868	1·4772	1·4690	1·4772	1·4852	1·4770	1·4849
Mol. wt. (ebullioscopic)	298	300	325	325	295	305	300
Wt % sulphur	<0·05	<0·05	<0·05	<0·05	<0·05	0·47	<0·05
Hydrocarbon Group Analysis							
% *Carbon in*:							
Aromatics	11·2	4·0	0·0	3·0	9·5	8·3	10·6
Naphthenes	37·2	43·0	38·0	41·0	41·0	30·0	35·8
Total rings	48·4	47·0	38·0	44·0	52·5	38·3	46·4
Paraffins	51·6	53·0	62·0	56·0	47·5	61·7	53·6
Silica Gel Analysis							
Wt % saturates	78·0	88·3	98·6	91·5	81·3	88·2	80·0
Wt % aromatics	22·0	11·7	1·4	8·5	18·7	11·8	20·0
IP 56 Oxidation Test							
Sludge wt %	0·84	0·72	0·05	0·56	0·71	0·61	0·78
Acid development (mg KOH/g)	1·27	1·05	2·85	0·88	0·96	0·87	1·05

TABLE III

Copper Solubility Test Results

Oil type	Wt % * aromatics	Copper concn, p.p.m.	Peroxide number, milli-equiv O/g †	Acidity, mg KOH/g
A	22·0	1·20	0·02	0·05
B	11·7	0·60	0·01	0·02
C	1·4	0·05	nil	0·02
D	8·5	1·55	0·02	0·05
E	18·7	0·20	0·02	0·03

* By silica gel analysis.
† Method of Kokatnur, V. R., and Jelling, M., *J. Amer. Chem. Soc.*, 1941, **63**, 1432.

Oils A, B, C, D, and E were tested for their ability to dissolve copper, with the results recorded in Table III. All the oils dissolved copper under the conditions of test. It is noteworthy that the solubility is lowest for the most highly refined oil (Oil C), and generally there is a relationship for the three oils from one crude (Oils A, B, and C) between copper solubility, peroxide number, and aromatic content, but this does not extend to oils from different crudes (Oils D and E). Oil E, in spite of a comparatively high aromatic content, dissolves only a small amount of copper.

The Effect of Further Refining on Copper Solubility

Various refining treatments intended to reduce or entirely eliminate any residual acidity which might have been responsible for the solution of copper metal were carried out using Oil A.

The results are shown in Table IV. Treatment of the oil with activated clay and/or aqueous alkali and distillation from solid caustic soda all reduced the tendency to dissolve copper, peroxide formation, and acidity of the oil, suggesting that the compounds responsible for the attack of the copper metal were acidic in character. In all cases these treatments reduced the acidity (as determined by IP 1/55A) of the oil before the solubility test to zero. Nevertheless, it was impossible to suppress completely the solubility of copper in the oil in any of these experiments.

In the case of oils inhibited with commercial oxidation inhibitors, no reduction of the copper solubility was found, although the usual decrease in acidity was observed (Table V).

Compounds capable of forming stable chelates with copper, *i.e.* potential deactivators, were next ex-

amined. In all cases the stable chelate of copper with the compound in question was prepared, and it was confirmed that the ion-exchange method [15] for the determination of soluble copper compounds was applicable to solutions in oil of copper complexed with the particular agent used.

The results reported in Table VI show that in no case was the dissolution of copper metal in the oil prevented by the chelating agent.

TABLE IV

Effect of Further Refining on Copper Solubility in Oil " A "

Additional treatment	Copper concn, p.p.m.	Peroxide number, milli-equiv. 0/g	Acidity, mg KOH/g
Nil	1·20	0·02	0·05
Treated with 1·5% activated clay, at 100° C	0·65	0·01	0·03
Washed with aqueous NaOH, water, and dehydrated with 1·5% activated clay at 100° C	0·25	0·01	0·01
Washed with aqueous NaOH, water, and dehydrated with magnesium perchlorate	0·80	0·01	0·04
Distilled from solid NaOH under reduced pressure	0·75	0·02	0·03
Distilled from solid NaOH under reduced pressure and treated with 1·5% activated clay at 100° C	0·35	0·01	0·02

TABLE V

Effect of Oxidation Inhibitors on the Solubility of Copper in Oil " A "

Inhibitor	Concn, wt %	Copper concn, p.p.m.	Peroxide number, milli-equiv. 0/g	Acidity, mg KOH/g
None	—	1·20	0·02	0·05
PBN	0·10	1·25	0·01	0·00
PBN	0·25	1·35	nil	0·01
DBPC	0·10	1·10	nil	0·00
24M6B	0·10	1·15	nil	0·00

Some additives, for instance disalicylal-propylenediamine, salicylaldoxime, and 8-hydroxyquinoline, notably increased the amount of copper going into solution under the conditions of test. Others showed little significant effect.

TABLE VI

Effect of Catalyst Deactivators on the Solubility of Copper in Oil " A "

Additive	Concn., wt, %	Copper conc, p.p.m.
Nil	—	1·20
Disalicylal-propylenediamine	0·05	5·95
Ethylenediamine	0·05	1·80
Salicylaldoxime	0·05	6·10
Anthranilic acid	0·05	1·30
Quinaldinic acid	0·05	1·65
8-Hydroxyquinoline	0·05	10·60

It is to be expected that oxidation products, such as hydroperoxides and acids, formed in the oil during the test would attack copper metal. The joint effect of a deactivator/conventional oxidation inhibitor combination was therefore studied. It was hoped that the deactivator would prevent the copper in solution from exercising a catalytic effect on the oxidation, while at the same time the oxidation inhibitor, by removing the free radicals formed in the primary oxidation reaction, would prevent the further formation of acidic compounds capable of attacking the copper metal. Thus, each additive would assist the other. The results of experiments on these lines, reported in Table VII, show that this hypothesis appears to be valid. In order to prevent dissolution of copper metal effectively under the test conditions,

TABLE VII

Effect of Oxidation Inhibitors and Catalyst Deactivators on the Solubility of Copper in Oil " A "

Inhibitor	Concn., wt %	Deactivator	Concn, wt %	Cu, p.p.m.	Acid dev., mg KOH/g	Peroxide number, milli-equiv. 0/g
—	—	—	—	1·20	0·05	0·02
PBN	0·1	—	—	1·25	0·00	0·01
DBPC	0·1	—	—	1·05	0·02	0·00
24M6B	0·1	—	—	1·15	0·02	0·00
PBN	0·1	Ethylenediamine	0·01	1·10	0·02	0·01
PBN	0·1	Disalicylal-ethylenediamine	0·02	1·10	0·04	0·00
PBN	0·1	Disalicylal-propylenediamine	0·02	3·95	0·02	0·00
PBN	0·1	*o*-Phenylenediamine	0·01	0·35	0·01	0·01
PBN	0·1	α-Picolinic acid	0·02	0·00	0·06	0·01
PBN	0·1	Quinaldinic acid	0·02	0·10	0·07	0·00
PBN	0·1	α, α′-Dipyridyl	0·02	0·60	0·02	0·01
PBN	0·1	Anthranilic acid	0·02	0·00	0·06	0·00
DBPC	0·1	,, ,,	0·02	0·05	0·10	0·00
24M6B	0·1	,, ,,	0·02	0·00	0·10	0·00
Phenothiazine	0·1	,, ,,	0·02	0·07	0·07	0·00
DBPC	0·1	Alizarin	$\ll$0·02	0·35	0·03	0·00
PBN	0·1	Mercaptobenzothiazole	0·02	0·30	0·02	0·00
PBN	0·1	α-Nitroso-β-naphthol	0·02	1·90	0·03	0·00
PBN	0·1	Diphenylcarbazone	<0·02	1·50	0·03	0·01
PBN	0·1	Picrolonic acid	<0·02	5·90	0·08	0·00
PBN	0·1	2,(2-Pyridyl)benzimidazole	0·02	0·00	0·00	0·01

Note: Alizarin, diphenylcarbazone, and picrolonic acid were not soluble to 0·02 per cent in the oil at room temperature, thus saturated solutions were used.

the simultaneous presence of an oxidation inhibitor and a deactivator is necessary.

Comparison of Tables VI and VII shows that in all cases the solubility of copper is reduced when inhibitor and deactivator are present simultaneously. In a number of cases, such as that of α-picolinic acid, anthranilic acid, and 2(2-pyridyl)benzimidazole, the dissolution of copper metal is practically eliminated by the combined action of the oxidation inhibitor and the deactivator.

DISCUSSION

It was found on a number of samples of oil from transformers working under comparatively arduous conditions that the soluble copper content was usually between 0·2 and 0·6 p.p.m.

In the laboratory, however, copper concentrations of up to 1·5–2·0 p.p.m. can be obtained at temperatures of 70°–80° C in 40–120 hours, while Liander,[1] working at temperatures of 100° C, dissolved even greater quantities of copper in oils, up to a concentration of 40 p.p.m. in 160 hours. On the basis of these results, it is rather surprising that the copper concentrations found in oils from service conditions are generally below 1 p.p.m. The reason for this is not clear, but the availability of oxygen may be an important factor.

Careful removal of traces of acidic compounds from an oil reduces the copper solubility considerably. It is likely, therefore, that acid attack is primarily responsible for the dissolution of the copper, and traces of acidic oxidation products present in the oil, or possibly dissolved by the oil from the insulation varnish, would be of importance in this connexion.

The effect of chelating agents in increasing the solubility of copper in oil (Tables VI and VII) may be due to a shift of the solubility equilibrium through the formation of the chelate. It may be significant that the salicylic acid derivatives, and 8-hydroxyquinoline, which form very stable copper complexes, show the greatest increases in copper solubility. In contrast, amino acids and diamines do not show this effect.

The combined effect of oxidation inhibitors and chelating agents of the aromatic amino acid–diamine type in radically suppressing the solubility of copper is surprising. The following experiment, carried out with anthranilic acid, indicates that the effect appears to be due to adsorption of the chelating compound on the copper.

In this experiment a copper foil, prepared in the standard manner, was treated with a solution of anthranilic acid in ether. The foil was removed from the solution, washed with ether, dried and then submitted to the copper solubility test as described previously, the oil being Type A, containing 0·1 per cent PBN. The dissolved copper, after 72 hours at a temperature of 70° C, amounted to only 0·1 p.p.m.

From this experiment one can conclude that the amino acid is strongly adsorbed (probably chemisorbed) on the copper, thus protecting the copper surface, and that the action of the anti-oxidant is to protect in turn the adsorbed layer from further oxidation. A further point supporting this view is that anthranilic acid and picolinic acid, which are very effective in preventing the dissolution of copper, have been proposed as anti-corrosive agents for copper.[18, 19]

This experiment also shows that the distinction between catalyst deactivators and catalyst passivators does not apply generally. Because of the formation of a stable and catalytically inert copper chelate anthranilic acid should be classified as a deactivator. However, according to the above results this compound also acts as a passivator.

THE EFFECT OF DEACTIVATOR/OXIDATION INHIBITOR COMBINATIONS IN PASSIVATION OF TRANSFORMER OILS

Having established that some chelating agents, in combination with oxidation inhibitors, can effectively suppress the dissolution of copper in transformer oils under laboratory conditions, a considerable number of such compounds was investigated for the passivation of transformer oils. Accelerated tests for sludge and acidity development, and oxygen absorption, were carried out.

All compounds were tested by IP 56 for acid development and sludge formation. These experiments were mainly carried out on Oil A, which shows a comparatively poor response to oxidation inhibitors. It was thought that this oil would be particularly useful in a screening test for deactivators, since their action would not be masked by the effect of the oxidation inhibitors. Results are quoted in Tables VIII and IX, which respectively record experiments in which deactivators were used alone and in conjunction with oxidation inhibitors. It will be noted that, of the deactivators used alone, only ethylenediamine and anthranilic acid showed an effect, and that generally greatly improved results were obtained when an oxidation inhibitor was present in the oil in addition to the deactivator.

The combinations of deactivator and oxidation inhibitors which were tested were divided into three groups (Table IX) according to their effectiveness as determined by this test. The most effective group consists of a number of aromatic amino acids and diamines,[20] whilst some commonly used chelating agents, such as ethylenediamine-tetra-acetic acid (in the form of the E.D.T.A. oleylamine salt) and disalicylal-ethylenediamine, are either ineffective or

TABLE VIII

Effect of Deactivators on Oil "A" in IP 56 Oxidation Test

(Deactivator concentration = 0·02% w/w)

Deactivator	Sludge, wt %	Acid dev.,* mg KOH/g
Nil	0·84	1·27
Ethylenediamine	0·36	0·64
Disalicylal-ethylenediamine	1·13	2·63
Hexamethylene-tetramine	0·92	1·34
Anthranilic acid	0·26	0·69
2(*o*-Hydroxyphenyl)benzoxazole	1·33	1·98
8-Hydroxyquinoline	1·37	2·54

* Correction was made, where necessary, for a small acidity of the oil when acidic deactivators were used. This applies to all figures for acidity development given in this paper.

TABLE IX

Combinations of Deactivators and Oxidation Inhibitors

IP 56 Oxidation Test

(Base Oil A; Deactivators: 0·02%; Oxidation inhibitor: 0·1%)

Deactivator	Oxidation inhibitor	Sludge, wt %	Acid dev., mg KOH/g
Base Oil and Oxidation Inhibitors			
—	—	0·84	1·27
—	PBN	0·59	1·18
—	DBPC	0·91	1·46
—	24M6B	1·26	1·80
(1) *Effective Combinations*			
Ethylenediamine	PBN	0·12	0·34
Anthranilic acid	PBN	0·06	0·15
Picolinic acid	PBN	0·12	0·11
o-Phenylenediamine (0·01%)	PBN	0·15	0·38
α,α′-Dipyridyl	PBN	0·08	0·19
o-Phenanthroline	PBN	0·14	0·13
Quinizarin	PBN	0·18	0·31
2(2-Pyridyl)benzimidazole	PBN	0·05	0·08
Benzotriazole	PBN	0·07	0·16
2-Amino-3-naphthoic acid *	PBN	0·05	0·11
(2) *Moderately Effective Combinations*			
Hexamethylene-tetramine	PBN	0·36	0·31
Nicotinic acid	PBN	0·21	0·21
Chrysazin	PBN	0·28	0·43
α-Nitroso-β-naphthol	PBN	0·25	0·39
Anthranilic acid	24M6B	0·25	0·49
" "	DBPC	0·22	0·61
" "	Phenothiazine	0·24	0·24
o-Phenylenediamine	24M6B	0·44	0·75
o-Amino-phenol	PBN	0·24	0·39
Laurylamine	PBN	0·29	0·61
Diethylhexylamine	PBN	0·29	0·65
Oleylamine/E.D.T.A. 0·1%	PBN	0·18	0·40
Alizarin *	PBN	0·34	0·67
Quinizarin	DBPC	0·38	0·50
N-N′-Ethylene-di-anthranilic acid *	PBN	0·48	0·84
(3) *Ineffective Combinations*			
Disalicylal-ethylenediamine	PBN	0·65	1·10
Disalicylal-propylenediamine	PBN	0·98	1·17
*iso*Nicotinic acid *	PBN	0·66	1·25
Methylanthranilate	PBN	0·87	1·21
Ethylanthranilate	PBN	0·67	1·24
n-Phenyl-anthranilic acid	PBN	0·75	1·59
8-Hydroxyquinoline	PBN	0·78	1·28
Salicylaldoxime	PBN	1·23	1·52
Phthalocyanine *	PBN	0·68	0·88
Picrolonic acid *	PBN	1·14	1·34
Mercapto-benzothiazole	PBN	1·34	1·50
Diphenylcarbazone	PBN	0·69	1·16
Diphenylthiocarbazone	PBN	1·09	2·00
Disalicylal-*o*-phenylenediamine	PBN	1·07	2·04
n-Benzoyl-phenylhydroxylamine	PBN	0·90	1·25
2(*o*-Hydroxyphenyl)benzoxazole	PBN	1·01	1·75
Phenylnaphthylformazylbenzene	PBN	0·77	1·34
1,2-Diamino*cyclo*hexane	PBN	0·80	1·54

* These compounds were not soluble to 0·02 per cent, and a saturated solution at room temperature was used for the test.

only moderately effective. A more detailed discussion of these results will be given later.

In Table X the authors have compared results obtained with deactivator/oxidation inhibitor combinations in the IP 56 oxidation test with those on copper solubility described earlier. In most cases the

TABLE X

Comparison of Oxidation Stability and Copper Solubility

Oxidation stability: IP 56 Oxidation test
Copper solubility: See p. 322 for test conditions
Oil: Type A
Oxidation inhibitor concentration: 0·1% w/w
Deactivator concentration: 0·02% w/w

Oxidation inhibitor	Deactivator	Cu, p.p.m.	IP Oxidation Test	
			Sludge, wt %	Acid dev., mg KOH/g
—	—	1·20	0·84	1·27
PBN	Ethylenediamine	1·10	0·12	0·34
PBN	Anthranilic acid	0·00	0·06	0·13
PBN	α-Picolinic acid	0·00	0·12	0·11
PBN	Quinaldinic acid	0·10	0·66	0·85
PBN	*o*-Phenylenediamine	0·35	0·15	0·38
PBN	α,α′-Dipyridyl	0·60	0·08	0·19
PBN	2(2-Pyridyl)benzimidazole	0·00	0·05	0·08
DBPC	Anthranilic acid	0·05	0·22	0·61
24M6B	" "	0·00	0·25	0·49
Phenothiazine	" "	0·00	0·24	0·24
DBPC	Alizarin *	0·35	0·59	0·42
PBN	Dalisalicyl-propylenediamine	3·95	0·98	1·17
PBN	Diphenyl carbazone	1·50	0·69	1·16
PBN	Picrolonic acid *	5·90	1·14	1·34
PBN	α-Nitroso-β-naphthol	1·90	0·25	0·39

* Not soluble to 0·02% w/w. Saturated solution used.

TABLE XI

Deactivator/Oxidation Inhibitor Combinations with Solid and Dissolved Copper

IEC test [21]
Oil "A." Temp: 100° C, 92 hr, O_2 at 1 l/hour
Oxidation inhibitor: 0·1% PBN
Deactivator concn.: 0·02%

Deactivator	Solid copper		Soluble copper (10 p.p.m.)	
	Sludge, wt %	Acid dev., mg KOH/g	Sludge, wt %	Acid dev., mg KOH/g
Nil	0·01	0·17	0·07	0·61
Ethylenediamine	0·02	0·07	0·32	1·84
o-Phenylenediamine	0·01	0·06	0·06	0·55
Anthranilic acid	nil	0·10	0·02	0·05
Quinaldinic acid	0·02	0·07	0·01	0·11
α,α′-Dipyridyl	0·01	0·06	0·15	0·11
α-Nitroso-β-naphthol	0·03	0·07	0·07	0·45
α′(2-Pyridyl)benzimidazole	0·03	nil	0·03	0·22

compounds effective in preventing dissolution of copper in oil also reduce sludge and acid formation on oxidation. Ethylenediamine, which does not suppress the dissolution of copper but shows a marked effect in IP 56, is an exception.

Table XI compares results obtained on application of the IEC test [21] using solid, and also soluble, copper catalysts at 100° C with oxygen passing through the oil at 1 litre/hour for 92 hours, the solid catalyst being a helix formed from 30·5 cm of 1-mm-dia copper wire (0·39 sq. cm. copper surface/g oil). Examination of the results shows that, when a solid copper catalyst

was used, those compounds found to be effective in the IP 56 oxidation test were also effective in this test. Moreover, most of these compounds were also effective in the presence of soluble copper, but there are exceptions, namely ethylenediamine, *o*-phenylenediamine, *a*-nitroso-β-naphthol.

Table XII contains further results on the performance of the anthranilic acid/PBN system, using solid and soluble copper, and soluble iron catalysts, in the IEC test.[21] In the case of the test with 10 p.p.m. of soluble copper, some of the catalyst must have been precipitated as copper anthranilate, since an independent test showed this compound to be soluble only to the equivalent of 2–3 p.p.m. copper in Type A oil at 70° C. An interesting point is the effect of anthranilic acid in the absence of an oxidation inhibitor, which is much more pronounced in this test than in the IP 56 test (see Table IX). This is probably due to the lower temperature of the IEC test and the less severe oxidation conditions.

The determination of the rate of oxygen absorption is now generally accepted as a valuable method for rating inhibited oils. Rates of oxidation can be determined at any stage of the reaction, and the

TABLE XII

Anthranilic Acid/Phenyl-β-Naphthylamine System

IEC test [21]

Conditions: as in Table XI

	Sludge, wt %		Acid dev., mg KOH/g	
	92 hr	164 hr	92 hr	164 hr
(1) 10 *p.p.m. Cu as Cu Naphthenate*				
No additive	0·10	0·13	0·50	0·56
Phenyl-β-naphthylamine, 0·1% w/w	0·06	0·09	0·61	0·20
Anthranilic acid, 0·02% w/w	0·02	0·03	0·10	0·14
PBN, 0·1% w/w + Anthranilic acid, 0·02% w/w	0·02	0·05	0·05	0·03
(2) 10 *p.p.m. Fe as Fe Naphthenate*				
No additive	0·05	0·09	0·50	0·29
Phenyl-β-naphthylamine, 0·1% w/w	0·04	0·06	0·13	0·36
Anthranilic acid, 0·02% w/w	0·02	0·02	0·01	0·01
PBN 0·1% w/w + Anthranilic acid, 0·02% w/w	0·01	0·02	0·01	0·01
(3) *Copper Wire*				
No additive	0·01	0·03	0·17	0·22
Phenyl-β-naphthylamine, 0·1% w/w	0·01	0·01	0·17	0·11
Anthranilic acid, 0·02% w/w	nil	nil	0·03	0·03
PBN 0·1% w/w + Anthranilic acid, 0·02% w/w	nil	0·01	0·10	0·12

method is particularly useful in determining the length of induction periods.

Further tests were therefore carried out using these techniques. On a variety of oils (as specified in Table II) the effect of an efficient combination of deactivator and oxidation inhibitor (PBN/anthranilic acid or DBPC/anthranilic acid) on the oxidation rate was compared with the effect of PBN and of DBPC alone.

In these tests two experimental methods were used. In the first, a static method, a quantity of the oil under test (10 g) containing either a solid or a soluble copper catalyst, was confined in a " Sligh " type flask in the presence of oxygen. The solid catalyst in this

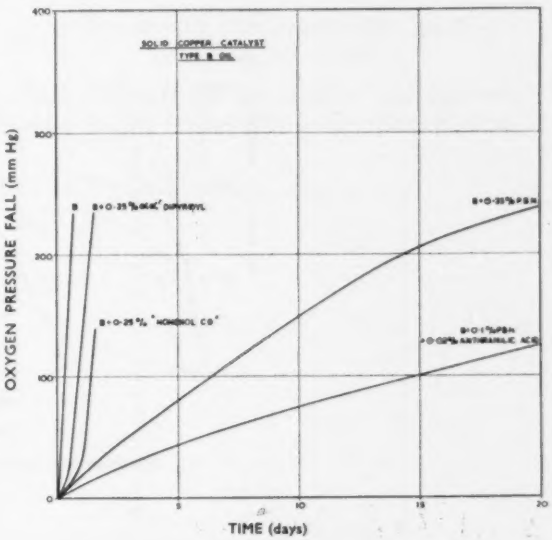

FIG 2

STATIC OXYGEN ABSORPTION TEST AT 120° C

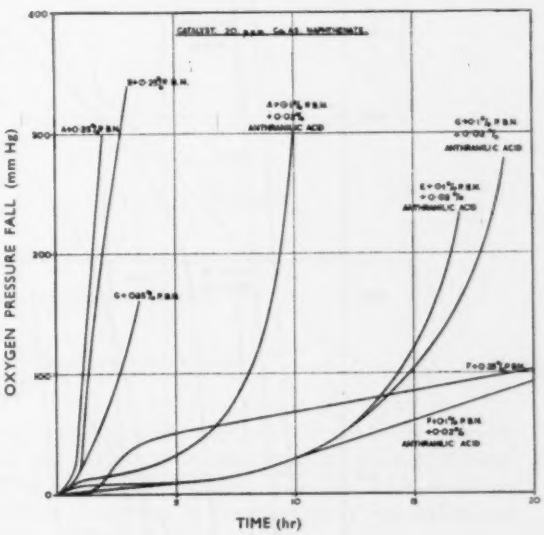

FIG 3

STATIC OXYGEN ABSORPTION TEST AT 100° C

case consisted of a helix of 1-mm-dia copper wire, 35 turns, 5·3 mm dia corresponding to 1·14 sq. cm. of copper surface/g oil. The rate of fall of oxygen pressure at a temperature of 100° or 120° C was determined. Typical curves are shown in Figs 2 and 3.

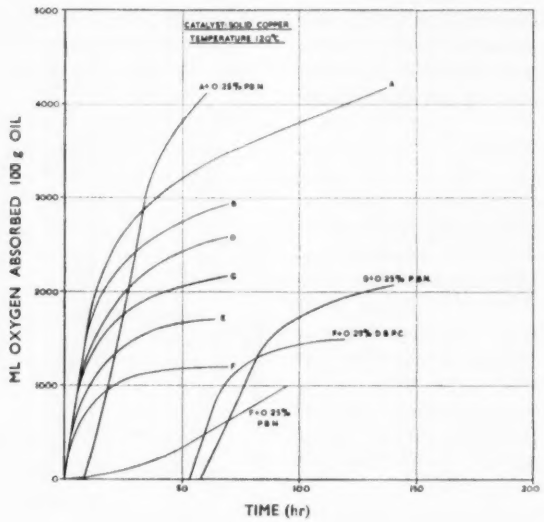

FIG 4

CIRCULATORY OXYGEN ABSORPTION TEST

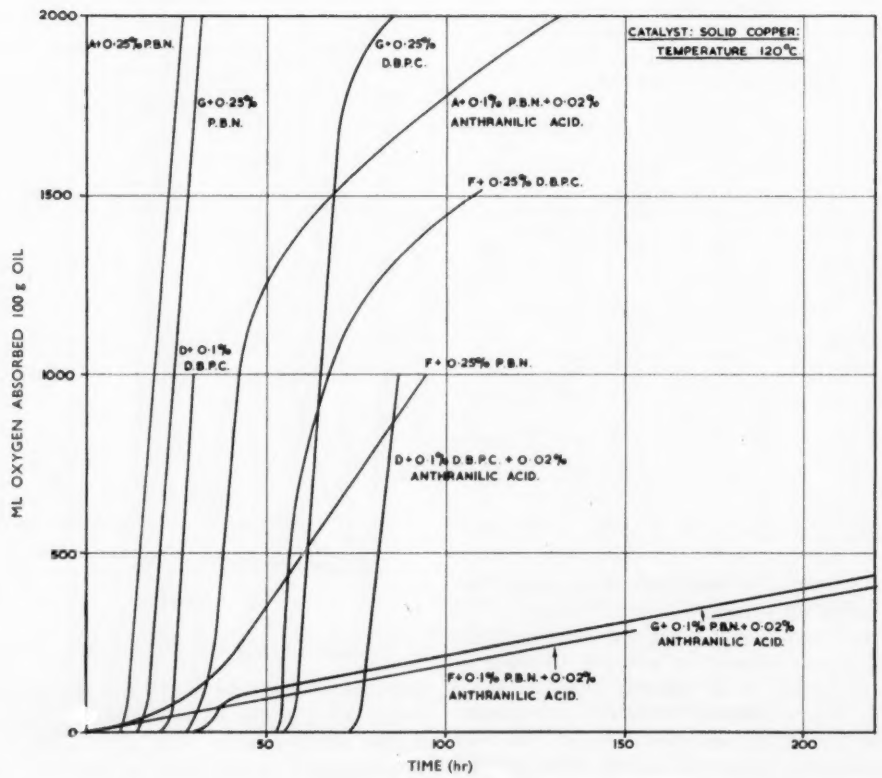

FIG 5

CIRCULATORY OXYGEN ABSORPTION TEST

The static technique has the drawback that only the earliest part of the oxidation reaction can be observed, corresponding to an oxygen absorption of approximately 140 ml/100 g of oil, and that oxygen diffusion will be at least partly a rate-determining factor. On the other hand, these objections are eliminated in the case of the circulatory apparatus, where oxygen is passed through the oil continuously and the volume of oxygen absorbed at constant pressure can be followed to any desired level of reaction.

quantity is considered, the passivated oils containing an oxidation inhibitor and a deactivator combined perform well.

COMPARISON OF INHIBITED AND PASSIVATED OILS

Using an anthranilic acid/oxidation inhibitor combination the authors have also compared the perform-

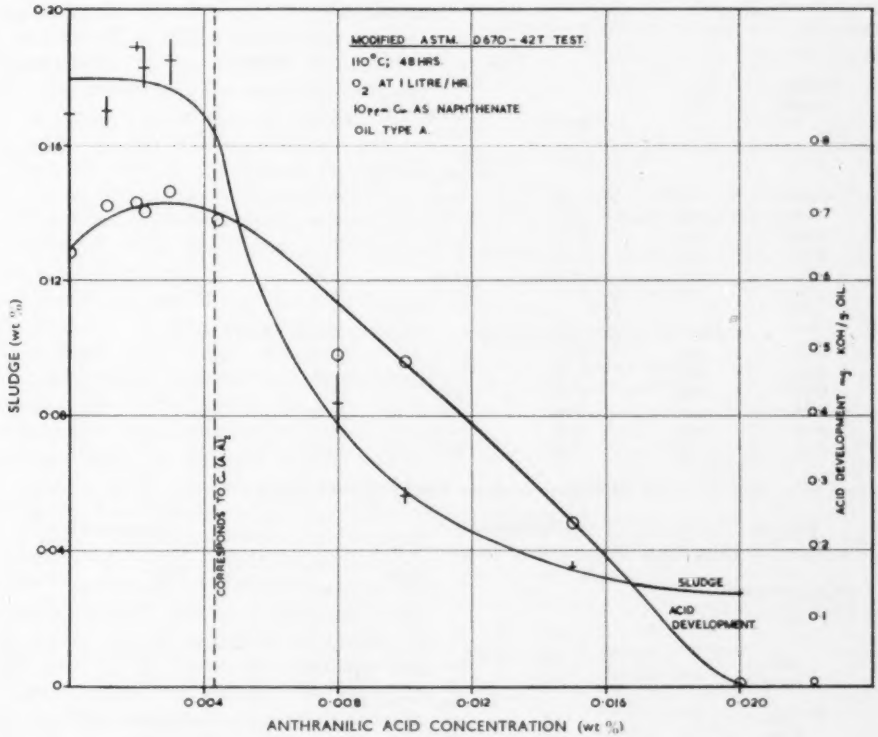

Fig 6

EFFECT OF ANTHRANILIC ACID CONCENTRATION ON PASSIVATION

Typical curves obtained on a circulatory apparatus, which was similar to the one described by Brook and Matthews,[22] are shown in Figs 4 and 5. In these experiments, 20 g of oil were used with a solid copper catalyst present in the form of the helix described above. Two helices were used in order to obtain the same ratio of 1·14 sq. cm/g oil. In most cases clearly defined induction periods are observed, but in some instances a slow oxidation with no break in the oxygen absorption/time curve was noted. For this reason, induction periods and the times required for the absorption of 1000 ml O_2/100 g oil are quoted (Table XIII). It will be noted that, particularly if the latter ance of passivated with that of inhibited oils, on the oils of Table II, in the IP 56 and the IEC [21] tests. These comparative results, together with those on oxygen absorption in the circulatory apparatus, are given in Table XIII.

DISCUSSION

It has been observed already that some of the chelating compounds most successful in other applications, such as di-salicylal-ethylenediamine (" Nonoxol CD "), disalicylal-propylenediamine (" Tenamene

60 "), and ethylenediamine-tetra-acetic acid (as the oil-soluble oleylamine salt) are of little or no value in the passivation of transformer oils. The explanation may be that these compounds are not stable under the conditions of the transformer oil accelerated oxidation tests.

Whatever the explanation for the failure of these anthranilic acid/PBN gives much better results. (Oil B was used as base oil, since it is comparable in oxidation stability with the one used by Dobry.)

According to the screening tests using Oil A in IP 56 (see Table IX), compounds which are successful deactivators belong to the group of aromatic amino acids, such as anthranilic acid, picolinic acid, and

TABLE XIII

Comparison of Inhibited and Passivated Oils

Oil	Base oil		Inhibited oil †				Passivated oil ‡	
			PBN		DBPC		Deactivator + PBN	
	Sludge, % wt.	Acid,* dev.	Sludge	Acid, dev.	Sludge	Acid dev.	Sludge	Acid dev.
IP 56 Oxidation Test								
A	0·94	1·17	0·37	0·83	0·52	1·18	0·05	0·16
B	0·72	1·05	0·14	0·24	0·04	0·32	0·08	0·20
D	0·56	0·88	0·30	0·85	nil	0·10	0·04	0·12
E	0·71	0·96	0·12	0·14	0·65	1·14	0·08	0·16
F	0·61	0·87	0·14	0·18	0·36	0·81	0·07	0·14
G	0·78	1·05	0·12	0·18	0·61	0·94	0·09	0·10
IEC Test [21] (*Catalyst* 5 *p.p.m.* Cu + 5 p.p.m. *Fe as Naphthenates*)								
A	0·17	0·51	0·17	0·72	0·10	0·10	0·03	0·07
B	0·14	0·62	0·03	0·06	0·01	0·04	0·01	0·00
D	0·11	0·60	0·02	0·05	0·01	0·05	0·02	0·01
E	0·15	0·53	0·06	0·21	0·02	0·11	0·03	0·01
F	0·12	0·52	0·03	0·06	0·01	0·04	0·03	0·00
G	0·11	0·43	0·12	0·02	0·02	0·16	0·01	0·02

Circulatory Oxidation Test (*Solid* Cu *Catalyst*)

Oil	Base oil	Inhibited oil †				Passivated oil ‡			
		PBN		DBPC		Deact. + PBN		Deact. + DBPC	
	ml O_2 absorbed/ 100 g oil at 70 hr	t_i	t_{1000}	t_i	t_{1000}	t_i	t_{1000}	t_i	t_{1000}
A	3500	9	19	—	—	28	42	—	—
D	2550	57	77	24 90	30 ** 95 ††	53	80	76	87
F	1250	—	95	53	67	—	>260	—	—
G	2200	14	24	55	64	—	>284	—	—

t_i = induction period in hours.
t_{1000} = time for absorption of 1000 ml O_2/100 g oil.
* acid development—mg KOH/g.
† inhibited oils—0·25% w/w inhibitor.
‡ passivated oil—0·02% anthranilic acid; 0·1% inhibitor.
** 0·1% inhibitor.
†† 0·25% inhibitor.

compounds as deactivators, it is not surprising that Dobry,[23] who used these and similar compounds to deactivate copper in transformer oil oxidation tests, obtained unsatisfactory results.

These conditions are further illustrated in Fig 2, which reproduces results obtained with solid copper as catalyst on an apparatus similar to that used by Dobry. It is clear that chelates of the type used by this worker are ineffective, whilst the combination of diamines such as *o*-phenylenediamine. The equivalent aliphatic diamines such as ethylenediamine still show a similar effect, but the *cyclo*aliphatic 1,2-diamino*cyclo*hexane is inactive.

Apart from the amino acids and the diamines, compounds containing certain nitrogen heterocyclic rings such as 2(2-pyridyl)benzimidazole and benzotriazole are also good deactivators. 2(2-pyridyl)-benzimidazole is interesting because it is effective

without the simultaneous presence of an oxidation inhibitor, probably because it acts as an efficient oxidation inhibitor itself.

Amongst the compounds (Table IX) of category (2), which are generally less effective than those of category (1), there is the oleylamine salt of E.D.T.A. as a derivative of a conventional chelating agent, aromatic hydroxyquinones such as alizarin, quinizarin, and also long chain amines such as laurylamine and diethylhexylamine. The latter type of compound containing only one electron-donating group no longer forms chelates, but is still able to complex copper.

Some structural effects which can be deduced from the results of Table IX are further illustrated in Table XIV. For instance, in the series picolinic acid, nicotinic acid, *iso*nicotinic acid (α-, β-, and γ-pyridine carboxylic acid), the deactivating efficiency declines markedly from the first to the last of these acids. This would correspond to the stability expected from a five-ring planar chelate (picolinic acid), a non-planar six-ring chelate (nicotinic acid), and a non-planar seven-ring (*iso*nicotinic acid).

Esterification of the acid group destroys the deactivating efficiency. In this case an inner complex salt could no longer be formed. Alkylation of the amino group also reduces the deactivating efficiency.

The deactivating effect of anthranilic acid was investigated further. It was confirmed in a more direct experiment that copper in the form of copper anthranilate is inactive as a catalyst, by preparing the copper/anthranilic acid chelate, and testing this compound in a concentration equivalent to 10 p.p.m. copper. The relevant experimental details are given in Table XV. As already mentioned, the solubility of the copper/anthranilic acid chelate in oils is only of the order of 2–3 p.p.m. calculated as copper. A considerable part of the copper anthranilate must therefore have remained undissolved. However, the experiment confirms the deactivating effect of anthranilic acid on soluble copper. This must take place either by forming the chelate in solution up to a concentration of 2–3 p.p.m. of copper or, if copper is present in still larger concentration, by precipitation of the excess copper complex.

In Fig 5 the deactivating effect of anthranilic acid as a function of the anthranilic acid concentration is given for a fixed concentration of 10 p.p.m. copper as naphthenate. Acid and sludge values were determined by the IEC test [21] and Oil A was used. It is seen that the deactivating effect becomes appreciable only after the stoichiometric ratio of 2 mol anthranilic acid per mol copper (0·0043 per cent anthranilic acid for 10 p.p.m. copper) has been reached. Beyond this concentration, acid and sludge development drop until deactivation becomes completely effective, when the anthranilic acid concentration reaches a value of about five times that required by the stoichiometric ratio.

If we now turn to the comparison of passivated (anthranilic acid/PBN system) and inhibited oils reported in Table XIII it is found that according to the tests measuring acidity and sludge (IP 56 and IEC) beneficial results are obtained on passivation of all the oils tested. However, it is also clear that no differentiation is possible on the basis of these results between appropriately inhibited and passivated oils.

TABLE XIV

Influence of Molecular Structure on Deactivating Action

(IP 56 Oxidation test; type A oil)

	Sludge, wt %	Acid dev., mg KOH/g
Base oil + 0·1% PBN . .	0·59	1·18
Chelating agent: 0·02%. *Anti-oxidant*: *P.B.N.* 0·1%		
INFLUENCE OF CHELATE RING STABILITY		
Picolinic (α) . . .	0·12	0·11
Nicotinic (β) acid . .	0·21	0·21
*iso*Nicotinic (γ) . . .	0·66	1·25
BLOCKING OF ACID GROUP		
Anthranilic acid . . .	0·06	0·13
Methyl anthranilate . .	0·87	1·21
Ethyl anthranilate . .	0·67	1·24
BLOCKING OF AMINO GROUP		
N-Phenyl-anthranilic acid .	0·75	1·59

TABLE XV

Catalytic Effect of Copper Anthranilate

IEC test [21]

Type A Oil; temp 110° C; oxygen at 1 l/hr for 48 hr; 0·005% w/w copper anthranilate = 10 p.p.m. Cu

	Sludge, wt %	Acid dev., mg KOH/g
0·1% PBN + 0·005% Cu anthranilate .	nil	0·03
,, + 10 p.p.m. Cu as naphthenate .	0·18	0·92
,, + 0·02% anthranilic acid + 10 p.p.m. Cu as naphthenate .	0·02	nil

Both types of oils perform so well that the limits of the tests are approached to such an extent that a satisfactory discrimination becomes impossible.

For a satisfactory graduation and comparison of passivated and inhibited oils, the results on the oxygen absorption test are of greater value (Table XIII and Figs 2 and 3). It is clear from these results that passivation is selective and that some oils respond much better than others.

The oxidation resistance of oil A, which does not respond well to inhibition by oxidation inhibitors, can be increased considerably by passivation; how-

ever, the resistance so achieved is still below that of inhibited Oil D, this oil showing good response to oxidation inhibitors. Passivation of Oil D does not increase the oxidation resistance beyond that of the inhibited oil, though at equal concentrations of oxidation inhibitor the passivated oil shows an advantage.

In the case of Oils F and G, however, the passivated oils show a marked increase in the oxidation resistance over that of the inhibited oils, although both oils (F and G) respond well to oxidation inhibitors, the oxidation resistance of the inhibited oils being similar to that of inhibited Oil D.

CONCLUSIONS

The fact that small but significant amounts of dissolved copper were found in all of fifty-six samples of used transformer oil which were tested together with the earlier evidence cited,[1-3] strongly supports the view that dissolved copper is generally present in these oils in concentrations of 0·2–0·6 p.p.m. and sometimes higher. This evidence is strengthened further by the results in the " copper solubility test," which at the same time demonstrate that oils from different crudes and/or refined by different methods differ considerably in their ability to dissolve copper. Traces of acidic compounds are an important factor promoting copper solubility.

Certain chelating agents in combination with oxidation inhibitors suppress dissolution of copper under the conditions of the solubility test. The effect appears to be due to adsorption of the chelating agent on the surface of the copper metal, indicating that these compounds can act as " catalyst passivators " as well as " catalyst deactivators."

Of the many combinations of chelating agents (catalyst deactivators) and oxidation inhibitors which were subjected to the IP 56 test, in one particular transformer oil an appreciable number were found of value. Very effective are combinations of aromatic amino acids or aromatic diamines with phenyl-β-naphthylamine or with ditertiary butyl-*para*-cresol. The combinations of anthranilic acid and one of these two oxidation inhibitors showed good results when used in a number of oils and in several of the accelerated tests. For a comparison of " inhibited " and " passivated " oils only the oxygen absorption test was sufficiently sensitive. The results in this test show that different oils vary in their response to passivation. Passivated oils prepared from base oils with good response to passivation show significantly better oxidation characteristics than inhibited oils made from base oils having a good response to oxidation inhibitors.

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THE SUSCEPTIBILITY OF OILS TO OXIDATION INHIBITORS *

By J. H. T. BROOK †

SUMMARY

The essential simplicity of the inhibited oxidation of oils has been demonstrated by correlating the reactivity of oils towards tert-butoxy free radicals (being a measure of the reactivity of the hydrogen atoms in the oils) with the reciprocal of the induction period observed when these oils, inhibited with phenolic inhibitors, are oxidized in laboratory oxidation tests.

It is generally agreed that there are three mechanisms by which oxidation inhibitors may work. The possible modes of action are by passivating or deactivating metal catalysts, by reducing peroxides, or by scavenging the free radicals which form the chain carriers in oxidation reactions. Many inhibitors may have a dual effect, *e.g.* many peroxide-reducing agents contain active sulphur atoms, and they may in addition passivate copper surfaces by causing a sulphide film to form and protect these surfaces.

Whilst it is impossible to review the many published articles on the mechanism of action of inhibitors in oils in a paper of this nature, it is possible to pick out several papers which illustrate the main trends of thought on this problem. It might be noted that Watson and Tom [1] have produced a particularly comprehensive review of metal deactivating inhibitors; Denison and Condit [2] were perhaps the first investigators to realize the peroxide-reducing character of sulphur compounds as oxidation inhibitors, and their line has been followed by several investigators. The studies of the mode of action of the phenols as radical capture agents are perhaps derivative from the work of Waters and his collaborators [3–5], Campbell and Coppinger,[6] Cook,[7] Bolland and ten Have,[8] and have been further developed by, for example, Bickel and Kooyman.[9]

Despite this quite extensive literature, there is little information to be found about the influence of the composition of the base oil on the properties of inhibited oils. It is this aspect which is considered in this paper.

It has been shown in an earlier paper [10] that reasonably simple kinetics were shown by the oxidation of a high viscosity index oil inhibited with a calcium phenate which it is believed acts solely as a radical capture agent. The proportionality between the reciprocal of the induction period and the iron or copper content when iron or copper stearates were used as catalysts, and between the reciprocal of the induction period and the square root of the oxygen pressure, suggested that the system the authors were working with was particularly simple, and the reactions would be written:

$$RH + O_2 \xrightarrow{Fe,Cu} RO_2\cdot \quad . \quad . \quad . \quad (1)$$

$$x\ RO_2\cdot + Inh \longrightarrow \text{inert products} \quad (2)$$

where RH represents a typical molecule present in oil. Free radicals are generated in a chain initiation reaction (reaction (1)) and are scavenged by the inhibitor (in unknown stoichiometry). Thus, during the induction period, the inhibitor is being steadily depleted, and the end of the induction period occurs when the inhibitor is totally consumed. If w_1 is the rate of reaction (1) and t_i the induction period

$$w_1\, t_i = x\,[Inh]$$

The rate of reaction (1) should depend upon the ease of breaking the R–H bond; it is well-known that the induction period at constant inhibitor addition depends upon the quality of the oil being inhibited. If an independent measure of the reactivity towards free radicals of the hydrogen atoms in oils can be shown to correlate with induction periods of inhibited oils in oxidation tests, this will be further evidence of the simplicity of the mechanism of inhibition of oils by radical-scavenging inhibitors.

Such an independent measure of the reactivity of the hydrogen atoms in oils may be obtained by measuring the butanol : acetone ratio in the products of decomposition of di-*tert*-butyl peroxide in oil. The reactions involved are [11, 12]

$$t\text{-BuOO}\ t\text{-Bu} \longrightarrow 2\ t\text{-BuO}\cdot$$

$$t\text{-BuO}\cdot + RH \longrightarrow t\text{-BuOH} + R\cdot$$

$$t\text{-BuO}\cdot \longrightarrow CH_3\cdot + CH_3COCH_3$$

As the last of these reactions probably proceeds at a rate independent of the hydrocarbon, this serves as an internal reference by which differences in the rate of the second reaction may be observed, and the butanol: acetone ratio is a measure of the reactivity of the compound RH.

EXPERIMENTAL

Two ranges of experimental oils were chosen for the investigation. The first comprised experimental insulating oils. Four of these are of the I.R.O. (Insulating Reference Oil) series, which have been distributed fairly widely by the International Electrotechnical Commission to laboratories concerned with insulating oil testing (see C. N. Thompson, this symposium), and the fifth was prepared from a similar crude, but has a higher aromatics content. These were inhibited with 0·3 per cent of 2,6-di-*tert*-butyl-4-methylphenol, and were oxidized in the static oxidation test of Beaven, Irving, and Thompson [13] at 120° C in the presence of 100 p.p.m. soluble copper (added as naphthenate). The second range comprised

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† "Shell" Research Ltd.

lubricating oils, chosen to cover oils from various crudes, rather than oils derived from the same crude but refined to different degrees. The twelve oils were chosen from stocks available in the laboratory, and they are derived, it is believed, from ten different crudes. These lubricating oils were inhibited with a calcium phenate [10] (to 2 meq Ca per 100 g oil) and oxidized in a circulatory oxidation apparatus at 160° with 50 p.p.m. of iron as catalyst, added as stearate.

It is necessary to point out that these twelve oils were chosen to display a range of inhibited oxidation stability though none is far removed from being a serviceable I.C. engine oil base-stock. Thus the variations in induction periods observed in the test should not be taken to reflect adversely or otherwise on the quality of the crude oil source.

Reaction with di-*tert*-butyl peroxide was effected by weighing 85 g of oil into a tube and washing the oil off the neck of the tube with 15 g of chlorobenzene (an inert diluent). The oil was degassed under vacuum, the tube cooled in solid carbon dioxide to solidify the contents, and 3·1 g of di-*tert*-butyl peroxide was added. The tube was re-evacuated whilst being kept cold, and sealed *in vacuo*. The peroxide decomposition was conducted by heating the tubes for five hours in an oil bath at 135° C.

The products were analysed by opening the tube and pouring the contents into a round-bottomed flask containing 30 ml of chlorobenzene. The volatile products were then distilled at a pressure of 20–40 mm Hg, and at temperatures up to 100° C into a receiver cooled by solid carbon dioxide. 20-ml portions of chlorobenzene solution were pipetted into a conical flask containing aqueous hydroxylamine hydrochloride and were analysed for acetone by titration with N/10 caustic soda using bromophenol blue indicator. Colorimetric comparison of the aqueous layer with a blank determination was necessary to locate the end point precisely. *Tert*-Butanol was analysed by pipetting 8 ml portions of the chlorobenzene solution into 50 ml concentrated hydrochloric acid. The mixture was shaken for 3 minutes to convert the butanol to butylchloride, then allowed to settle. A 5-ml portion of the chlorobenzene layer was then taken by pipette and saponified in a pressure bottle. Chloride ion was determined by Volhard's method. Comparative blank determinations were run.

TABLE I

Comparison of Reactivity towards t-BuO· and Oxidation Induction Period for Insulating Oils

Oil	Induction period in test (hours)	Chain initiation rate *	*t*-BuOH acetone	Aromatics content, %wt
I.R.O. 3 .	51	0·020	8·2	5·6
I.R.O. 4 .	48	0·021	8·3	9·8
I.R.O. 5 .	25	0·040	8·6	17·9
I.R.O. 2 .	14	0·072	9·0	27·0
Oil A . .	9·4	0·106	9·7	34·0

* Chain initiation rate expressed as the reciprocal of the induction period.

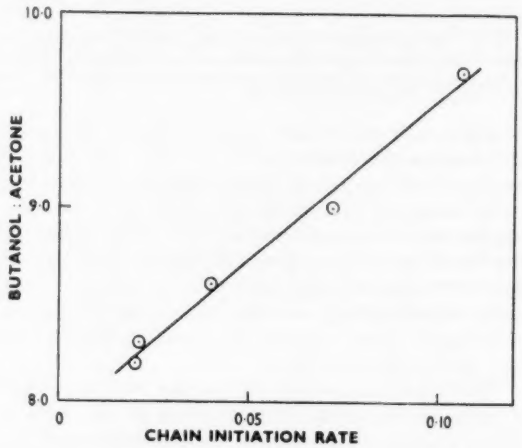

FIG 1. INSULATING OILS

RESULTS

The results of the tests on the five insulating oils are shown in Fig 1 and Table I.

As mentioned above, oil A is an insulating oil prepared from a similar crude to that used for the preparation of the other oils, but being more aromatic, it is less stable to inhibited oxidation. The results show a good correlation between the butanol : acetone ratio and the chain initiation rate. However, as this may merely reflect the aromatics content of the oil, the aromatics possibly being similar in character in all the oils, a more crucial test of the hypothesis is provided by the results reported in Table II and shown in Fig 2, where the test oils were gathered from various sources and where the constitution of the oils could be very different.

TABLE II

Comparison of Reactivity towards t-BuO· and Oxidation Induction Period for I.C. Engine Lubricating Oils

Oilfield, source of oil	Induction period in test (minutes)	Chain initiation rate	*t*-BuOH acetone
U.S.A., oilfield No. 1 . .	45	0·022	15
U.S.A., oilfield No. 1 . .	85	0·012	12
U.S.A., oilfield No. 2 . .	95	0·011	11
U.S.A., oilfield No. 3 . .	140	0·0071	9·6
U.S.A., oilfield No. 4 . .	110	0·0091	9·2
U.S.A., oilfield No. 5 . .	170	0·0059	9·0
Venezuela, oilfield No. 6 .	265	0·0038	8·9
Middle East, oilfield No. 7 .	210	0·0048	8·8
Venezuela, oilfield No. 8 .	150	0·0067	8·6
Venezuela, oilfield No. 6 (desulphurized) . . .	260	0·0038	8·5
Venezuela, oilfield No. 9 .	245	0·0041	8·4
Middle East, oilfield No. 10	160	0·0062	8·0

Once again, it may be noted that these oils are not necessarily best-quality oils which can be obtained from the particular crudes. For example, quite fortuitously, the oils from U.S. crudes appear to have lower inhibited oxidation stability than those from the Venezuelan crudes. Aromatics contents are unfortunately not available on these oils.

Fig 2 shows a correlation between the chain initiation rates in the oxidation test and the butanol : acetone ratio. The correlation appears to be less satisfactory than that shown in Fig 1, but this is probably not really the case, since the errors in the determination of the chain initiation rate are of the order of ± 5 per cent and in the determination of the butanol : acetone ratio of the order of ± 10 per cent.

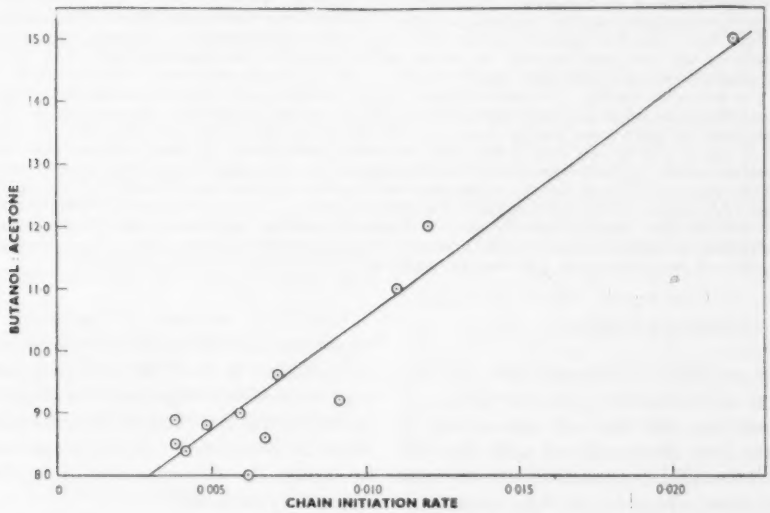

FIG 2. LUBRICATING OILS

DISCUSSION

The correlation of the reactivity of the hydrogen atoms in the constituents of insulating and lubricating oils with the chain initiation rate as measured by techniques using inhibitors lends strength to the view previously expressed that the inhibited oxidation is a simple chemical system, in which free radicals are generated catalytically, and react with the inhibitor until all the inhibitor is removed. However, notice should be taken of the limits of the demonstration: working with such oils as were available, the author could only use the range of butanol : acetone ratios from 8 to 15, and the accuracy of the work permits only the suggestion of linear correlation. If this correlation should exist over a wider range of hydrogen-atom reactivities and chain-initiation rates, then it might well not be linear.

Although it would seem reasonable to suppose that hydrocarbons with a labile hydrogen atom (as measured, for example, by the butanol : acetone ratio) would be undesirable components of insulating or lubricating oils, some caution should be used before the results of the correlation are in any way extrapolated: the present work really may be taken to justify further use of induction period measurements with phenolic and probably amine inhibitors as a measure of chain initiation rates. The results may further be taken to show that progress in applying chemical kinetics to the complex problem of the oxidation of oils is, in fact, feasible, since if the oxidation conditions are properly chosen, the oxidation of oils appears to be little more complicated than the oxidation of a simple mixture of pure hydrocarbons.

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B B

THE OXYGEN ABSORPTION CHARACTERISTICS OF INHIBITED TRANSFORMER OILS *

By L. MASSEY † and A. C. M. WILSON †

SUMMARY

The static oxygen absorption test has been studied as a method for assessing the oxidation stability of inhibited oils and a favourable opinion formed thereon. Using this test, commercial and laboratory-blended oils have been examined at various inhibitor concentrations, catalyst concentrations, and temperatures. It is suggested that the test period required to reach an absorption of 300 ml O_2 per 100 g oil (termed the " useful life period ") is the best single criterion of an oil.

Conclusions reached are: the efficiency of inhibitors and the response of oils to inhibition vary widely; useful life period is approximately proportional to inhibitor concentration; induction period and post-useful life period at high catalyst concentrations may or may not depend on inhibitor concentration according to the nature of the oil and inhibitor; induction period is independent of catalyst concentration; the rate of oxidation of an oil after the inhibitor has been used up may be greater at low catalyst concentrations than that of the base oil; oils exhibit characteristic temperatures above which the rate of oxygen absorption increases only slowly and below which it decreases rapidly; the replenishment of the inhibitor in a used oil at the end of the induction period restores the oil to its original condition with respect to oxidation stability; the mixing of oils containing different inhibitors in many cases results in loss of efficiency; the static test is suitable for the assessment of used inhibited oils as well as new oils, it has some value for uninhibited oils, and it can be used with metallic copper as well as soluble copper; commercial oils available about 1955 show large differences in their oxidation characteristics; the possibility of further advances is indicated by a recent expreimental oil which gives an outstanding useful life period with soluble copper; the relative rating of oils is influenced by test conditions.

The static test has been used to examine some turbine oils and has enabled comparisons not readily possible by other methods to be made. In particular, it revealed that advances had been made in the oxidation resistance of the base oils and that these were still further improved by the addition of anti-oxidants.

INTRODUCTION

THE availability of inhibited transformer oils has created problems of evaluation and prediction of performance in service. As these oils are required to be produced from base oils complying with the provisions of B.S. 148 : 1951 for uninhibited oils and differ from the base oils only in the characteristics conferred by the inhibitor, assessment can be confined to a study of oxidation characteristics or any other factors related to the presence of inhibitors.

In the U.K. the satisfactory performance over very long periods of oils meeting the requirements of B.S. 148 has created confidence in the oxidation test (identical with IP 56) of that specification as a method of assessing their oxidation stability. Similarly, long experience shows that the methods in common use for determining the condition of an oil in service, and which the BSI intends to publish in the form of a code of practice for the maintenance of insulating oils, are dependable and satisfactory.

The problems with inhibited oils arise from the fact that their oxidation behaviour differs materially from that of uninhibited oils, and hence the methods established for the latter are not wholly applicable to the former. The difficulties of assessment are enhanced by the lack of long service experience with these oils, on which correlation between laboratory evaluation and service performance can be based.

Conclusive evidence of suitability lies in service experience, and several programmes of field tests have been started in the U.K. by oil suppliers, by oil users, and by research organizations associated with these interests, but it is likely to be some years before these tests are completed. In the meantime it is desirable to explore the characteristics of the oils by short-term laboratory methods.

In the laboratories of Metropolitan-Vickers inhibited oils were first examined by IP 56 and useful data were obtained, but its limitations became apparent and alternative methods were sought.

The most promising methods were considered to be those in which oxygen absorption is continuously recorded, *e.g.* the equipment described by Dornte [1] in 1936. The evaluation of inhibited oils by apparatus of this type has been described in recent years by Ham and Thompson,[2] Beaven, Irving, and Thompson,[3] Stoker and Thompson,[4] and Childs.[5] Such equipment falls into two classes, the circulating type on the Dornte principle, in which oxygen is passed through the oil, and the static type developed by Button and Davies,[6] in which oxygen is in contact with a static oil surface. The static test was finally chosen for the present programme on the grounds of its simplicity, reliability, and short duration.

Many oils have been examined by the static method, and the results obtained form the principal subject matter of this paper. Some results of oxidation tests by IP 56 are also given.

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The objectives of the present work were as follows:

(1) To study the behaviour of oils containing named inhibitors by means of the static oxygen absorption test under various conditions of temperature, catalyst concentration, and inhibitor concentration. By this approach it was hoped to establish the behaviour pattern of these inhibitors and to furnish data by which the results of the static test might be extrapolated to transformer operating conditions.

(2) To examine the results of adding additional inhibitor to artificially aged inhibited oils to furnish data by which the condition of a used oil can be assessed, and to explore the practicability of adding further inhibitor to an oil approaching the end of its service life.

(3) To study the behaviour of mixed inhibitors such as may be encountered in practice if transformers have to be topped up, or if they are filled either intentionally or accidentally with oils from different suppliers.

(4) To examine by the methods evolved from the foregoing studies, and by IP 56, the behaviour of commercial inhibited oils and to assess their relative merits.

Although the work was undertaken primarily for the evaluation of transformer oils, it has a bearing on inhibited turbine oils, and the characteristics of several of these oils have been determined by the static test.

METHODS USED

(1) *The IP 56 Oxidation Test*

This well-established test, operating for 45 hours at 150° C, needs no description. Its application to inhibited oils has been criticized on the grounds that the fixed oxidation time yields no precise information regarding the induction period and that it operates at a temperature considered to be too high for commonly used inhibitors. The former objection is undeniable. The latter may be considered by some oil users to be a criticism of the inhibitor and not of the test. Transient hot spot temperatures of the order of 150° C are not impossible in transformer windings under fault conditions, and may result in thin films of adjacent oil reaching similar temperatures. Furthermore, as one of the applications of inhibited oil is for transformers operating under abnormally severe conditions, the possession of a good factor of safety with respect to temperature is a not unreasonable requirement for such an oil.

When early inhibited oils were examined by IP 56 it was found that they fell into two groups, one consisting of oils giving negligibly low sludges and acid values, and the other of oils giving results not much less than those obtained on uninhibited oils.

It was believed that the test was discriminating between oils having an induction period longer than 45 hours and those which either possessed an induction period of less than 45 hours or incorporated inhibitors which were thermally unstable or volatile at 150° C. The value of this arbitrary division into two classes was challenged, and it was claimed that oils which yielded unsatisfactory results under the severe conditions of IP 56 would exhibit excellent characteristics in service. This may well be the case, but until conclusive field test data are available it was the authors' opinion that more confidence could be placed in the service performance of the class yielding negligible sludge and acidity than in the class showing little evidence of inhibition when examined by IP 56.

(2) *The Static Oxygen Absorption Test*

This test continuously records the oxygen absorbed by an oil, and so enables both the induction period and the subsequent rate of oxidation to be plotted. A diagram of the apparatus is given in Fig 2. A thin layer of oil is contained in a flat-bottomed, conical flask and maintained at a constant temperature in an oil bath. The flask is flushed with oxygen and then connected to the oxygen limb of an electrolytic cell in a U-tube with the electrolyte level adjusted to be slightly below the tip of the oxygen electrode when the oxygen pressure is slightly above atmospheric pressure. As oxygen is absorbed during the test the pressure falls and the electrolyte rises and makes contact with the electrode; oxygen is then liberated, and the rise in pressure depresses the electrolyte until contact with the electrode is broken and oxygen generation ceases. The process of make-up continues throughout the oxidation period. (The hydrogen evolved in the second limb escapes to atmosphere.)

The U-tube cell is connected electrically in series with a second cell in which the evolved hydrogen and oxygen are collected together in a sealed pressure chamber. As the two cells are in series, the gas pressure in the second chamber is proportional to the oxygen absorbed by the oil. The pressure is recorded continuously on a chart and calibrated against the volume of oxygen absorbed by the oil. The apparatus used was based on that developed by Button and Davies [6] and is shown in Figs 1 (*a*) and 1 (*b*). The various items are mounted on a reversible panel for ease of operation and economy of space. The oil bath, oxidation flask, and electrolytic cells are shown in Fig. 1 (*a*) and the pressure recorder in Fig 1 (*b*).

The provision made in the original form of the static equipment [3] and in the circulating equipment as used by Childs [5] for the absorption of water and carbon dioxide formed by oxidation has been omitted from the present apparatus as being an unnecessary and troublesome complication. It is not operative during the induction period, and it does not remove all the

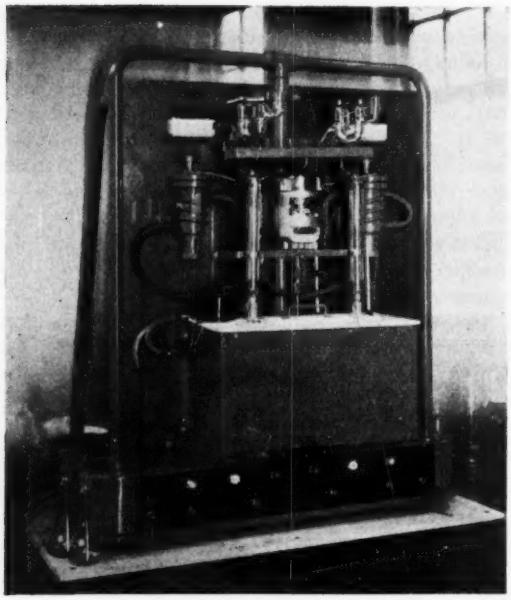

FIG 1 (*a*)

STATIC ABSORPTION APPARATUS—REACTION FLASK ASSEMBLY

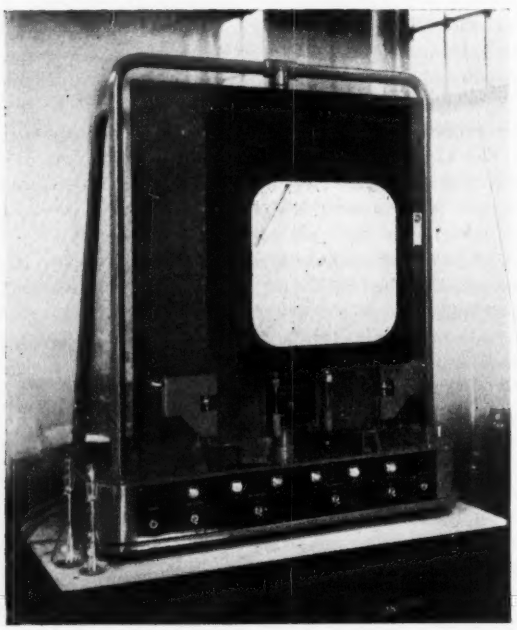

FIG 1 (*b*)

STATIC ABSORPTION APPARATUS—RECORDER

products of oxidation produced in the subsequent oxidation period. Indeed, its omission makes the test correspond more closely to transformer conditions.

The test conditions chosen by Beaven, Irving, and Thompson were 5 g of oil containing 100 p.p.m. of soluble copper and a temperature of 120° C. Results obtained using these conditions have also been reported by Childs, and it was desirable that the present work should continue to use them as basic reference conditions. The test when carried out under these conditions is referred to hereafter as the basic static test. Many experiments were, however, carried out at different temperatures and catalyst concentrations, as indicated on the respective graphs.

The repeatability obtained is approximately the same as that found by Beaven, Irving, and Thompson, *i.e.* about ± 5 per cent of the mean result, and there is some evidence that the reproducibility is not much worse. Many of the figures are the result of duplicate

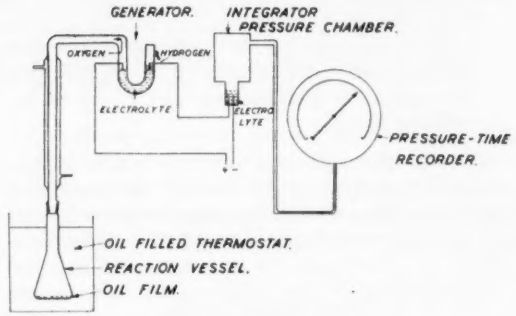

FIG 2

DIAGRAM OF STATIC ABSORPTION APPARATUS

tests. Others are single test results, but are confirmed by their position in regularly changing sequences of conditions.

Correlation between the results of the static absorption test and those of several other test methods has been established by Irving and Bravey.[7]

A full appreciation of the behaviour of an oil can be obtained only from a study of its oxygen absorption graph, but it is convenient to recognize three numerical results:

(*a*) The induction period. The time (in hours) from the start of the experiment to the point at which the rate of oxidation, as assessed by inspection, ceases to be very small and begins to increase rapidly with time.

(*b*) The useful life period. The time (in hours) from the start of the experiment to the point at which 300 ml O_2 per 100 g oil have been absorbed.

(*c*) The post-useful life period. The time interval (in hours) between the values of 300 and 1000 ml O_2 absorption per 100 g oil.

The useful life period owes its name and definition to the following considerations:

Some oils containing anti-oxidants exhibit clearly identifiable induction periods, but others absorb oxygen at a slow and regularly rising rate and an induction period cannot be recognized.

The induction period is a satisfactory measure of the initial oxidation period for the former class, but it is not applicable to the latter, and to provide a common index a small but measurable value of oxygen absorption must be chosen as the termination of the initial period. A suitable value would be one reached by oils of the former class shortly after the end of the induction period. If it is practicable to select this value so that it corresponds with the maximum degree of oxidation permissible in an oil in service, then the period terminated by this value, in addition to providing a numerical description of the initial portion of the absorption curve, will also provide some indication of the service rating of an oil and can appropriately be termed the " useful life period."

It is commonly accepted in the U.K. that a safe limit for the working life of an uninhibited oil in service is reached when the acid value has attained 1 mg KOH/g oil and, in the absence of evidence to the contrary, this value was considered applicable to an inhibited oil. It was therefore necessary to find the oxygen absorbed corresponding to such an acid value. A number of inhibited and B.S. 148 oils were subjected to the static test in the presence of both metallic and soluble copper catalysts and their acid values determined either before filtration or after precipitation and filtration of the sludge.

The acid value–absorption curve derived from these tests (Fig 3) shows that the oils reached a mean acid value of 1·0 mg/g at an absorption of 300 ml O_2 per 100 g oil.

The dependence of this curve on tests employing soluble copper in some cases and metallic copper in others is justified by the possible presence of both catalyst forms in transformers, but the inclusion of results on filtered and unfiltered oils needed careful consideration. The acidities of the unfiltered oils (*i.e.* the total acidities) were determined on the 5 g of oil in the oxidation flask and therefore contained any sludge present. The filtered oils contained no sludge. Neither of these procedures conform to established practice, for it is the custom to determine the acidity of a used oil on a sample as drawn from the transformer tank. This rarely contains suspended sludge, for this will have settled to the bottom of the tank, but it may contain dissolved sludge.

When sludge was present in the experimental oils the filtered oils gave lower results than the corresponding unfiltered oils, due to the removal of acidic sludge, and the difference between the two results increased with the degree of oxidation. However, at an oxygen absorption of 300 ml O_2 per 100 g oil the two values coincided, showing the absence of sludge. In addition, it was observed that at this value the oils were on the borderline of turbidity and that suspended sludge became increasingly apparent as the absorption increased beyond this point. The acid value at an absorption of 300 ml O_2 per 100 g oil was therefore not influenced by the inclusion of results on filtered oils, and may be considered to correspond closely to industrial practice. This value was therefore adopted as the termination of the useful life period.

Beaven, Irving, and Thompson [3] found that it needed an absorption of 650 ml O_2 per 100 g oil to produce an acid value of 1·0 mg/g, but they used oils covering a much wider range of degrees of refinement

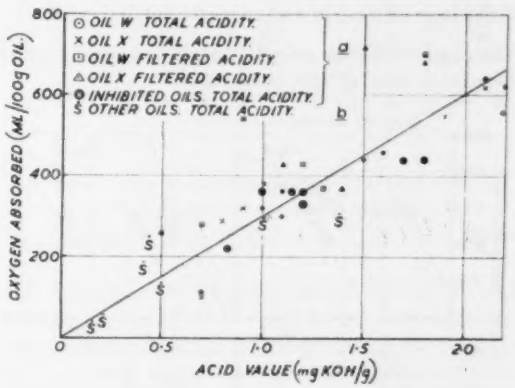

FIG 3

OXYGEN ABSORPTION–ACID VALUE

(*a*) Soluble copper catalyst (100 p.p.m.)
(*b*) Metallic copper catalyst (5 sq. cm.)

than the oils reported in Fig 3, and their determinations were made on filtered oils. The discrepancy is presumably associated with these differences in conditions.

It will be appreciated that the useful life period of an oil may be made up almost wholly of the induction period, or wholly of an oxidation retarded period, or of any combination of these two types of anti-oxidant influence. It must also be emphasized that the term " useful life period " is applied only to the static test results and not to the useful life of an oil in a transformer, which is described as " service life."

The post-useful life period represents a degree of oxidation not normally encountered in transformers, but it is a convenient means of expressing the slope of the absorption curve after the useful life period has been passed.

By the use of these three characteristics, *i.e.* induction period, useful life period, and post-useful life period, the essential features of any oxygen absorption curve can be expressed as three numbers.

RESULTS OF INVESTIGATION

(1) *Characteristics of Laboratory-blended Oils*

The oxygen absorption characteristics, using soluble copper catalyst, of oils containing named inhibitors were systematically explored. In addition, a limited number of static absorption tests with metallic copper and some IP 56 oxidation tests were made.

Four oils conforming to B.S. 148 and three well-known inhibitors were chosen:

Oils

W, an oil very similar in general characteristics to the base oil of commercial inhibited oil *F*.

X, an oil widely used in transformers.

Y, an oil very similar in general characteristics to the base oil of commercial inhibited oil *G*.

Z, the base oil used in commercial inhibited oil *B*.

(The commercial oils referred to are described later in the section dealing with these oils.)

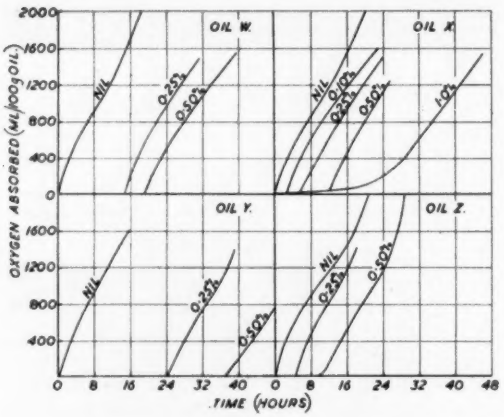

FIG 4

OXYGEN ABSORPTION–PBN CONCENTRATION

120° C—100 p.p.m. soluble copper

Inhibitors

PBN Phenyl-β-naphthylamine (Pure chemical-BDH)

24M6B 2,4-dimethyl-6-tertiary-butyl-phenol (Topanol A-ICI)

DBPC 2,6-ditertiary-butyl-*para*-cresol (Topanol O-ICI)

(The final column indicates the source of the particular sample of inhibitor used.)

(a) *The Static Absorption Test with Soluble Copper Catalyst*

The results of the static tests using soluble copper catalyst are dealt with in the following order: the influence of the inhibitor on the shape of the absorption curve, coupled with the influence of inhibitor concentration; the influence of temperature; and the influence of catalyst concentration.

The basic test conditions were 120° C, 0·25 per cent inhibitor, and 100 p.p.m. of soluble copper, and only

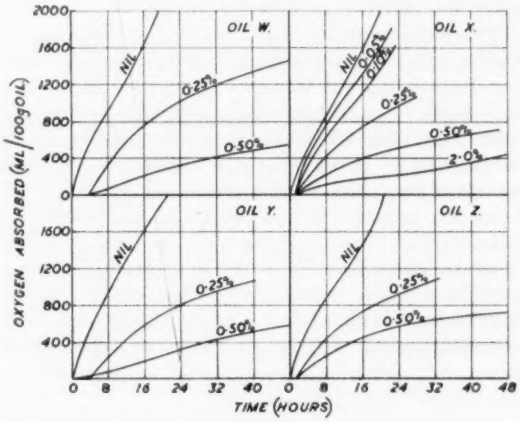

FIG 5

OXYGEN ABSORPTION–24M6B CONCENTRATION

120° C—100 p.p.m. soluble copper

one of these conditions was varied at a time. The individual curves for one variable are first presented, to be followed by two graphs relating useful life period and post-useful life period to the variable examined, the data for these graphs being taken from the individual absorption curves.

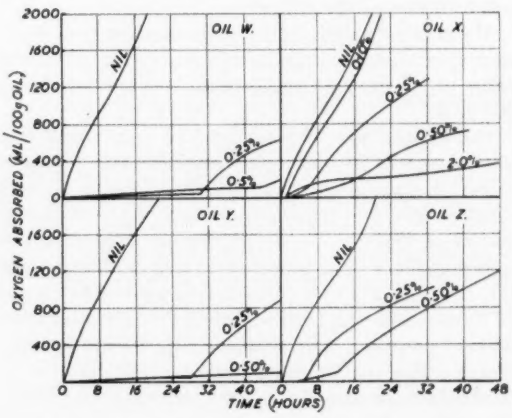

FIG 6

OXYGEN ABSORPTION–DBPC CONCENTRATION

120° C—100 p.p.m. soluble copper

Influence of the Inhibitor and its Concentration. The static absorption curves for the four B.S. 148 oils containing various concentrations of PBN, 24M6B, and DBPC are given in Figs 4–6. The graphs include as reference lines the absorption curves for

the base oils without inhibitor. These are smooth curves starting from the origin, each having a post-useful life period characteristic of the particular oil at the temperature and catalyst concentration used (*i.e.* 120° C and 100 p.p.m.).

The curves of the PBN blends are characterized by a substantial induction period dependent in duration on PBN concentration and a post-useful life period independent of concentration and almost identical with that of the base oil from which the blend was prepared. The duration of the induction period for a given PBN concentration and the proportionality between this period and concentration differ from oil to oil.

For the blends with 24M6B the induction periods are very short and independent of concentration, but the post-useful life periods increase with increasing inhibitor concentration and are in all cases greater than those of the base oils.

The DBPC blends show no common pattern, except that the post-useful life periods are in all cases greater than those of the base oils. The blend of DBPC with oil *X* behaves as all the blends of 24M6B, *i.e.* it has a negligible induction period independent of concentration and a post-useful life period varying with concentration. The blends of DBPC with oils *W*, *Y*, and *Z* possess induction periods and post-useful life periods both varying with concentration, and therefore combine the patterns of PBN and 24M6B blends.

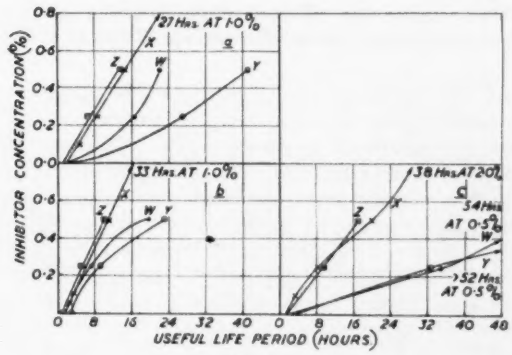

FIG 7

INHIBITOR CONCENTRATION–USEFUL LIFE PERIOD

120° C—100 p.p.m. soluble copper

(*a*) PBN blends (*b*) 24M6B blends (*c*) DBPC blends

The impossibility of using the induction period as a common measure of performance for all oils is emphasized by the different patterns of inhibitor response shown to exist in the blends examined. The useful life period takes account of all these forms of response and enables all the blends to be compared. The plots of useful life period against inhibitor concentration (Fig 7) show three forms: (i) the useful life period is directly proportional to concentration, *e.g.* oil *X* with PBN; (ii) the ratio of useful life period to inhibitor concentration decreases with increasing concentration, *e.g.* oil *W* with PBN; and (iii) this ratio increases with concentration, *e.g.* oil *Y* with 24M6B. No great error would be involved, however, in making a generalized statement that for each of the inhibited oils examined the useful life period is directly proportional to inhibitor concentration over the range economically feasible.

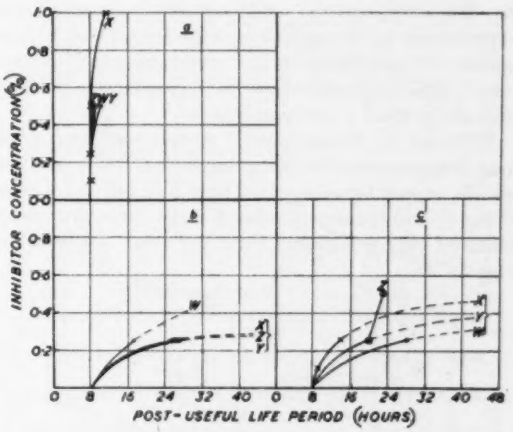

FIG 8

INHIBITOR CONCENTRATION–POST-USEFUL LIFE PERIOD

120° C—100 p.p.m. soluble copper

(*a*) PBN blends (*b*) 24M6B blends (*c*) DBPC blends

The influence of inhibitor concentration on the post-useful life periods of the oils is shown in Fig 8, which emphasizes the independence of post-useful life period from concentration for the PBN blends. The dependence on concentration shown by the 24M6B blends takes the form of small changes at the lower concentrations followed by rapid increases with concentrations above about 0·25 per cent. Above this value the curves depend on extrapolated points, which must be viewed with reserve but which indicate the trend. With DBPC the forms of the curves up to 0·25 per cent inhibitor are similar to those for 24M6B, but above this value they differ widely according to the base oil used.

The order of response to inhibition of the four oils as assessed by the useful life period is the same for all three inhibitors at 0·25 per cent concentration, *i.e.* *Z*, *X*, *W*, *Y*, the last-named being the most responsive, and this order is maintained up to at least 0·5 per cent concentration. The magnitude of the response varies considerably with the particular blend, the shortest useful life recorded with 0·5 per cent inhibitor being 10 hours for *X* and *Z* with 24M6B, the longest being greater than 50 hours for oil *Y* with

DBPC. The range of useful life period given by the four oils varies for each inhibitor, 24M6B giving the smallest range and DBPC the greatest.

From the information gained in the above tests an inhibitor concentration of 0·25 per cent was chosen for the temperature and catalyst concentration experiments as the optimum value for differentiating between the inhibited oils in a reasonable experimental time. This concentration is approximately that frequently used in commercial oils.

Influence of Temperature. Absorption curves at four temperatures in the presence of 100 p.p.m. of soluble copper for each of the four B.S. 148 oils appear in Fig 9, and similar families for the three groups of inhibited oils containing 0·25 per cent inhibitor in Figs 10–12.

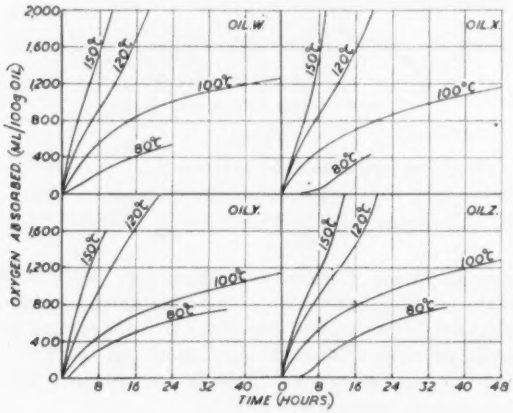

FIG 9

OXYGEN ABSORPTION–TEMPERATURE

B.S. 148 oils—100 p.p.m. soluble copper

These curves show that the general pattern of response exhibited in the inhibitor concentration experiments persists at all temperatures throughout the range explored, although it is in some cases modified.

The graphs indicate the existence of a limiting temperature for the first appearance of an induction period. For the base oils it is about 80° C, but for the inhibited oils it is above 150° C. The rate of increase of the induction period with decrease in temperature below 150° C varies with individual blends, *e.g.* at 120° C some PBN and some DBPC blends develop long periods, but all 24M6B blends still have short periods; between 100° and 80° C all inhibited oils develop long periods.

The plots of temperature against useful life period (Fig 13) are all asymptotic with knees which occur at a mean temperature of about 85° C for the base oils and about 115° C for the inhibited oils. Above these temperatures the useful life periods fall slowly to approximately a common value at 150° C. Below these temperatures the curves flatten rapidly and approach the horizontal, so that in this region the useful life period and the differences between the oils increase greatly with small decreases in temperature.

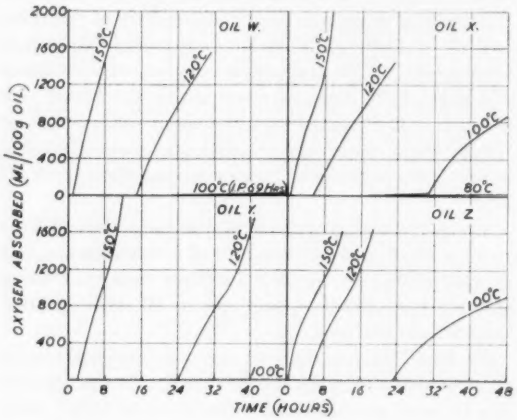

FIG 10

OXYGEN ABSORPTION–TEMPERATURE

0·25% PBN blends—100 p.p.m. soluble copper

In two cases temperature-useful life period curves cross. In one the differences involved are probably within the experimental error, but, in the other, oil *Z* with 24M6B crosses all its associated curves and the effect is significant. This result prevents a generalization that relative useful life periods of oils at 120° C

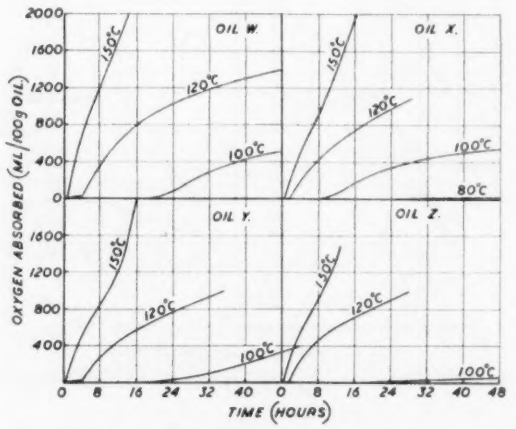

FIG 11

OXYGEN ABSORPTION–TEMPERATURE

0·25% 24M6B blends—100 p.p.m. soluble copper

are indicative of the relative performance at lower temperatures, although this is true for the majority.

In the majority of the plots of useful life period against temperature three points only were available

for the construction of the curves. This is open to criticism, but it was dictated by the time available for the work. It is believed, however, that it can have involved only minor errors in the form of the curves between 150° and 100° C.

In the plots of post-useful life period against temperature, the post-useful life periods lie within a close range for each group of oils. The base oils and the PBN blends exhibit a knee at 110° C and a post-induction period of 15 hours. For the 24M6B and DBPC blends the corresponding values are 115° C and

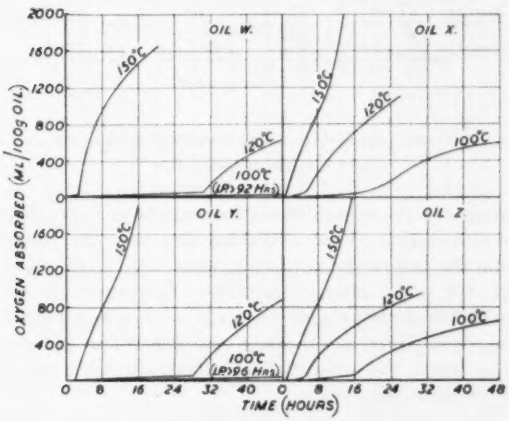

FIG 12

OXYGEN ABSORPTION–TEMPERATURE

0·25% DBPC blends—100 p.p.m. soluble copper

25 hours. This supports an earlier conclusion that 24M6B increases the post-useful life period, whereas PBN does not. For a number of these plots only two points were available, the useful life periods being so long that the post-useful life period was not reached, but the curves were completed by analogy with those for which these points were available.

With one exception the order of response of the oils to all inhibitors is the same at all temperatures, *i.e.* *Z*, *X*, *W*, and *Y*, the last-named being the most responsive. The exception is *Z* with 24M6B, and the behaviour of this blend in crossing its associated curves results in a complete reversal of its position, so that it becomes the oil most responsive to 24M6B at 100° C.

The temperature experiments show that the most suitable temperature for the determination of useful life period is 120° C. Above this temperature oils tend to approach a common value, below it the test period becomes impractically long. This confirms the choice of 120° C by Beaven, Irving, and Thompson in their original standardization of conditions. For a more complete examination suitable test temperatures are 110°, 120°, and 130° C.

Influence of Soluble Copper Concentration. These tests were carried out at 120° C, the inhibited oils containing 0·25 per cent of inhibitor. The absorption curves for the B.S. 148 oils are given in Fig 15 and

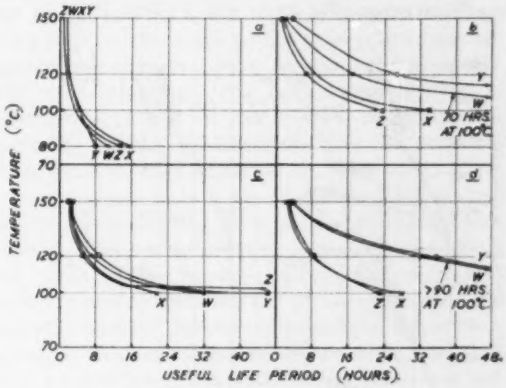

FIG 13

TEMPERATURE–USEFUL LIFE PERIOD

100 p.p.m. soluble copper

(*a*) B.S. 148 oils (*c*) 0·25% 24M6B blends
(*b*) 0·25% PBN blends (*d*) 0·25% DBPC blends

for the three groups of inhibited oils in Figs 16–18. Each of the B.S. oils yields a family of smooth curves starting from the origin and with post-useful life periods dependent on catalyst concentration. The

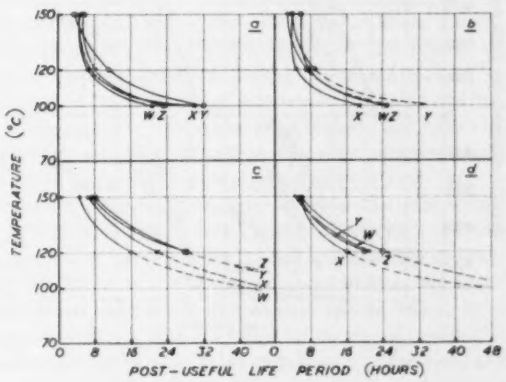

FIG 14

TEMPERATURE–POST-USEFUL LIFE PERIOD

100 p.p.m. soluble copper

(*a*) B.S. 148 oils (*c*) 0·25% 24M6B blends
(*b*) 0·25% PBN blends (*d*) 0·25% DBPC blends

inhibited oils exhibit induction periods which are independent of, or change only slightly with, catalyst concentration, and post-useful life periods which depend on concentration. The magnitude of the influence of concentration and the differences between the oils are best illustrated by the plots of useful life

period and post-useful life period against concentration.

The useful life periods hardly change for any of the oils at catalyst concentrations above 100 p.p.m., which therefore correspond to nearly maximal catalytic effectiveness (Fig 19). (Oil *Y* with PBN is an exception, and the useful life period changes appreciably from 100 to 200 p.p.m.) Below 100 p.p.m. the periods increase with decreasing catalyst concentration with knees present which occur over a range from 20 to 60 p.p.m., the rate of change varying for each oil with a general trend which suggests that very large differences may exist between the oils at low concentrations. The practical independence of the induction period on catalyst concentration means that changes in the useful life period are wholly dependent on retardation of the oxidation rate over the period from the end of the induction period to the 300 ml O_2 per 100 g oil absorption point. Consequently the useful life periods remain at a constant value when the induction period is the major component and increase only when the retardation component becomes of appreciable magnitude.

The curves for post-useful life period against concentration (Fig 20) are also asymptotic, the knee occurring in the concentration region 20–120 p.p.m. Below 50 p.p.m. for the base oils and PBN blends, and 100 p.p.m. for the 24M6B and DBPC blends, the curves depend on extrapolated points and on the general evidence of trends obtained on one or two selected oils at concentrations down to 10 p.p.m.

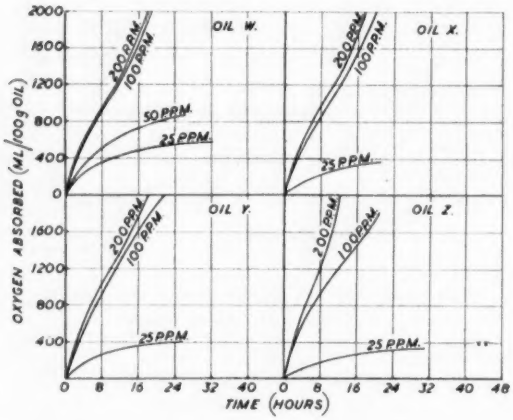

Fig 15

OXYGEN ABSORPTION–CATALYST CONCENTRATION

B.S. 148 oils—120° C

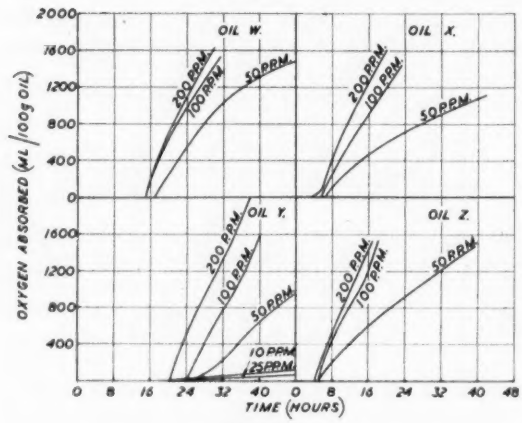

Fig 16

OXYGEN ABSORPTION–CATALYST CONCENTRATION

0·25% PBN blends—120° C

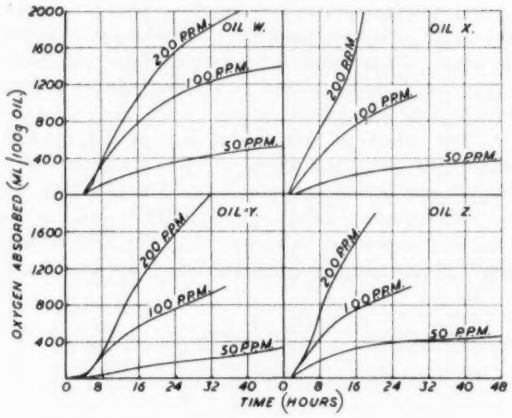

Fig 17

OXYGEN ABSORPTION–CATALYST CONCENTRATION

0·25% 24M6B blends—120° C

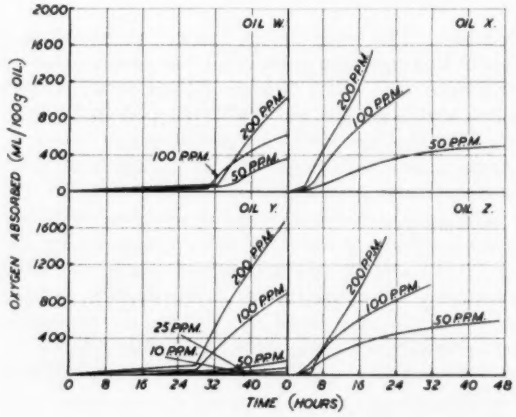

Fig 18

OXYGEN ABSORPTION–CATALYST CONCENTRATION

0·25% DBPC blends—120° C

The prediction of performance at very low concentrations is therefore difficult, but it appears certain that at low concentrations this period will be very long and the oils will differ very greatly.

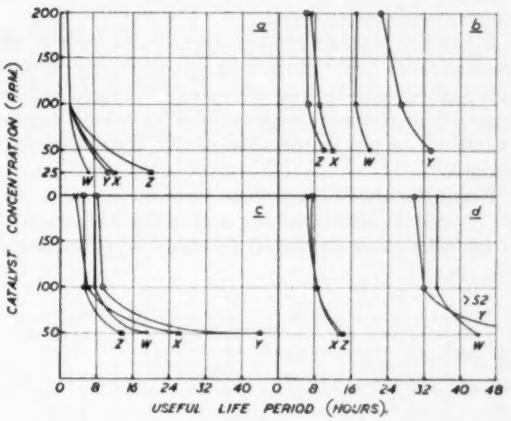

FIG 19

CATALYST CONCENTRATION—USEFUL LIFE PERIOD
120° C

(*a*) B.S. 148 oils
(*b*) 0·25% PBN blends
(*c*) 0·25% 24M6B blends
(*d*) 0·25% DBPC blends

There is a point of considerable importance revealed by the curves for post-useful life period. Fig 20 shows that the post-useful life periods of many inhibited oils increase less rapidly with decreasing

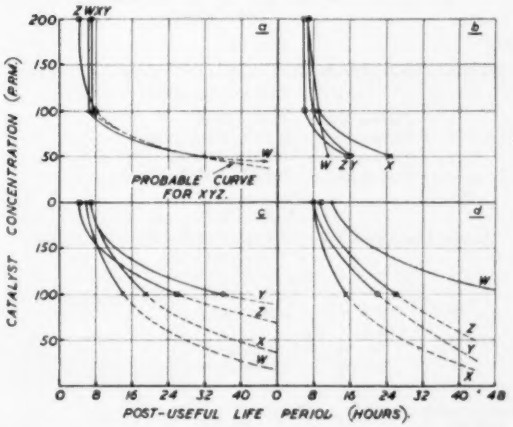

FIG 20

CATALYST CONCENTRATION—POST-USEFUL LIFE PERIOD
120° C

(*a*) B.S. 148 oils
(*b*) 0·25% PBN blends
(*c*) 0·25% 24M6B blends
(*d*) 0·25% DBPC blends

catalyst concentration than those of their base oils. As a result, the PBN blends, which at 100 p.p.m. have post-useful life periods equal to those of their base oils, yield values at 50 p.p.m. less than those of the base oils, *i.e.* the rate of oxidation of these oils after the inhibitor has been used up is faster than that of the base oil.

The post-useful life periods of the other inhibited oils, which at 100 p.p.m. are greater than those of the base oils, do not fall below those of their base oils at 50 p.p.m., but the trend of the extrapolated curves suggests that this may occur for some blends at still lower concentrations. This behaviour, however, is not universal, *e.g.* oil *W* with DBPC maintains the superiority of the inhibited oil over its base oil throughout the range explored.

These findings have a bearing on articles dealing with the performance of oils in service stating that the induction period is followed by a runaway oxidation rate. This has been attributed to inhibitor characteristics or to contamination of the oil during long periods in service. In the presence of inhibitors, it has been suggested, the contaminants are inactive, but they become active when the inhibitor has been used up. It seems unlikely, however, that contaminants picked up in service will be stronger catalysts than the high concentration of soluble copper used in the static test, and the present data suggest that the effect when present is a characteristic of the particular oil–inhibitor combination.

The order of response of the oils to inhibition in the basic static test was *Z*, *X*, *W*, and *Y*, and this order was substantially maintained over the inhibitor concentration and temperature ranges explored. This order, however, is not maintained at all catalyst concentrations, and some reversals occur at lower values. Consequently, although the choice of 100 p.p.m. of soluble copper catalyst in the basic static test is justified on the grounds of maximal catalytic activity, it is open to the criticisms that it does not rate the useful life periods of the oils in the same order of merit as those given at lower concentrations and that it swamps the large differences between the oils which are present at these lower concentrations. As the prediction of performance under transformer operating conditions is one of the primary objectives, these are serious objections to the basic static test. It is suggested that a concentration of 50 p.p.m. would be preferable, for at this value significant differences are present in a reasonable test period which are likely to be reflected in the performance of the oils at still lower concentrations.

The value of 50 p.p.m. is not suitable for the determination of post-useful life periods, and produces a less easily recognized end to the induction period than 100 p.p.m., so that for these purposes the latter is still to be preferred. In a full evaluation of an oil the recommended concentrations for useful life period are 75, 50, and 25 p.p.m.

The conclusions concerning the greater suitability of a concentration of 50 p.p.m. were reached late in the

course of these investigations, and in consequence, although the lower concentration is recommended, the majority of the results in this paper for the soluble copper static test have been obtained using the original concentration.

(b) *The Static Absorption Test with Metallic Copper Catalyst*

The oils were examined by the static test in the presence of metallic copper in order to compare the catalytic behaviour of the metal with that of soluble copper. There was not sufficient time available to make a systematic investigation of the influence of the various factors such as was made with soluble copper, and a limited number of tests was carried out using a single set of conditions. These conformed to those of the basic static test, except for the replacement of soluble copper by metallic copper and the choice of a temperature giving a convenient level of results.

As the comparison had to be based on one set of conditions for the metallic copper experiments, it was decided to select a copper area which approached maximal effectiveness and to compare the results obtained with those given by the maximal concentration of soluble copper. Liander and Ericson [8] showed that for the IEC test the copper area became rather less critical for many oils above a mass/area ratio of 1 : 1. For IP 56 the ratio employed is 3 : 1, and this has been shown to be beyond that at which the area–oxidation products curves flatten for some B.S. 148 oils.[9] The maximum area which could conveniently be accommodated in the static oxidation flask was found to be 5 sq. cm., *i.e.* a mass/area ratio of 1 : 1. Taking into consideration the available information and the physical limitations of the oxidation flask, the area of 5 sq. cm. appeared a reasonable choice and was adopted.

The information gained from comparisons at maximal values may have limitations with respect to the performance of oils in service. It has been shown that differences develop in the relative behaviour of oils as the concentration of soluble copper is decreased from the maximal value to those present in service, and similar differences will develop as copper area is decreased. On the other hand, the mass/area ratio of oil to copper to be found in transformers is not so well defined as the concentrations of soluble copper, which have been well established. For example, in an oil-impregnated coil wound from paper-covered copper conductors the oil permeates the paper and the mass/area ratio of the oil in the paper to surface area of copper conductor is far less than is used in any oxidation test. The adverse influence of this condition is limited by the restriction imposed by the paper on the movement of the oil and by the absence of oxygen other than that dissolved in the oil and paper, but some oxidation is nevertheless possible under these conditions of low mass/area ratio. On the other hand, the main bulk of the oil in the cooling system is exposed to little, if any, metallic copper. Taking these factors into consideration, the suggested test ratio of 1 : 1 may well be a reasonable starting point for practical comparisons.

It was found that inhibited oils gave no measurable absorption at 120° C with 5 sq. cm. of copper, but at 150° C the useful life periods were of the same experimentally convenient order as those for soluble copper at 120° C. A test temperature of 150° C was therefore adopted.

Using the above conditions, three of the base oils, *W*, *X*, and *Y*, and these oils containing 0·25 per cent of inhibitor, were examined for their oxygen absorption (Fig 21).

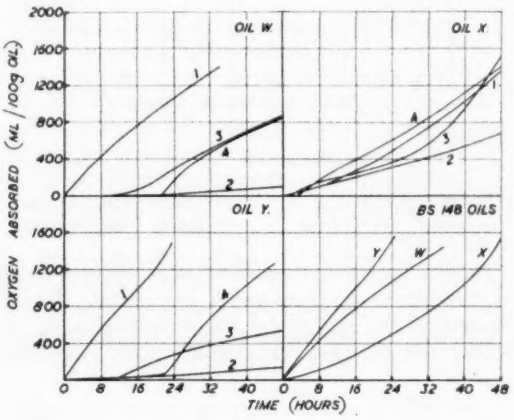

FIG 21

OXYGEN ABSORPTION WITH METALLIC COPPER CATALYST
150° C—5 sq. cm. copper
Curve No. 1—B.S. 148 oil
Curve No. 2—0·25% PBN blend
Curve No. 3—0·25% 24M6B blend
Curve No. 4—0·25% DBPC blend

TABLE I

Static Absorption Characteristics of Metallic and Soluble Copper Catalysed Oils

Catalyst	Temp °C	Base oil	Useful life period, hours			
			Base oil	Base oil + 0·25% PBN	Base oil + 0·25% 24M6B	Base oil + 0·25% DBPC
Metallic copper 5 sq. cm.	150	*W*	5	⩾50	24	27
		X	16	23	20	12
		Y	4	⩾50	26	25
Soluble copper 100 p.p.m.	120	*W*	2	17	6	35
		X	2	8	6	8
		Y	2	27	8	32
Soluble copper 50 p.p.m.	120	*W*	4	20	19	44
		X	6	11	26	19
		Y	6	34	44	>50

Table I lists the useful life periods for metallic copper and for soluble copper at concentrations of 100 and 50 p.p.m., enabling the following comparisons to

be made between the results of the static test for these catalyst conditions:

(i) Metallic copper is in general a less active catalyst at 150° C than soluble copper at 120° C.

(ii) With metallic copper oils *W* and *Y* are less stable than oil *X*. With soluble copper at 100 p.p.m. and, probably, also at 50 p.p.m., the three oils are equally stable.

(iii) With metallic copper *W* and *Y* respond strongly to the three inhibitors, but the response of *X* is weak. With soluble copper the three oils respond strongly to the three inhibitors, but in general *W* and *Y* respond more strongly than *X*.

These general statements have been kept concise to present the more important comparisons in a simple form. Other comparisons are as follows: for the oils with DBPC, metallic copper and 100 p.p.m. of soluble copper are roughly equal in their catalytic activity; with all oils 24M6B decreases far more rapidly in efficiency with increase in soluble copper concentra-

TABLE II

IP 56 Tests on Laboratory-blended Oils

Inhibitor	Oil								
	W			*X*			*Y*		
	Sludge, %	Acid value, mg/g	Sludge + acids, %	Sludge, %	Acid value, mg/g	Sludge + acids, %	Sludge, %	Acid value, mg/g	Sludge + acids, %
None	0·89	1·5	1·49	0·85	1·2	1·25	0·88	1·7	1·45
0·25% PBN	0·13	0·25	0·21	0·48	0·6	0·68	0·21	0·7	0·44
0·5% PBN	0·07	0·17	0·13	0·42	0·6	0·62	0·10	0·3	0·20
1·0% PBN	—	—	—	0·43	0·7	0·66	—	—	—
0·25% 24M6B	0·38	1·2	0·78	1·25	1·4	1·72	0·40	1·2	0·8
0·5% 24M6B	0·45	1·1	0·82	1·14	1·3	1·51	0·21	0·9	0·57
2·0% 24M6B	0·03	0·2	0·10	0·55	—	—	0·05	0·3	0·13
0·25% DBPC	0·00	0·2	0·07	0·99	1·2	1·39	0·08	0·8	0·35
0·5% DBPC	0·00	0·1	0·03	0·85	1·4	1·32	0·00	0·2	0·07
2·0% DBPC	—	—	—	0·01	0·4	0·14	—	—	—

TABLE III

Characteristics of Commercial Inhibited Transformer Oils

Test	Criteria	Results on oils								
		A	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*X* *
Static Soluble copper at 120° C	Induction period	2·5	5	1·5	29	27	34	18	49	None
	Useful life period	4	7	4	32	32	38	20	51	2
	Post-useful life period	7	7	10	13	78 ‡	18	9	5	8
Static Soluble copper at 150° C	Induction period	0·25	0·75	0·25	3	2·25	3	1·25	—	None
	Useful life period	2	1·25	2·25	3·75	3·75	4	2·5	—	1·5
	Post-useful life period	5·75	3·25	7·5	3·75	3·5	3·5	4	—	3·25
Static Metallic copper at 150° C †	Useful life period	49	22	—	80 ‡	27	32	80	—	18
	Post-useful life period	§	7	—	§	§	26 ‡	§	—	20
IP 56 Modified using soluble copper	Sludge	1·15	1·59	—	0·86	0·77	1·07	1·16	—	1·24
	Acid value	1·7	3·0	—	2·3	2·5	2·8	2·6	—	2·9
	Sludge + acids % ‖	1·75	2·59	—	1·66	1·57	1·97	2·06	—	2·24
IP 56 Standard (metallic copper)	Sludge	0·16	0·36	0·64	0·01	0·03	0·01	0·08	None	0·85
	Acid value	0·35	0·65	1·0	0·2	0·5	0·05	0·2	0·05	1·2
	Sludge + acids % ‖	0·28	0·58	0·97	0·08	0·20	0·03	0·15	0·02	1·25

* Uninhibited oil included for comparison.
† Absorption tests at 120° C using metallic copper gave no measurable absorption.
‡ Values obtained by extrapolation.
§ Values are high and cannot reasonably be obtained by extrapolation.
‖ The percentage of acids is calculated on the assumption that their mean molecular weight is 180.

tion than the other two inhibitors; the oxidation of oil *X* is accelerated by DBPC in the presence of metallic copper.

(c) *The IP Oxidation Test*

An examination by IP 56 of the laboratory-blended oils was made to assess these oils under a different set of test conditions and to provide data for the interpretation of the results obtained by this method during the examination of commercial oils reported later.

The results are given in Table II, which includes a column for the sum of the weights of sludge and acids formed.

For a given oil the sludge plus acid figure tends to remain constant with increasing inhibitor concentration until a limiting concentration is reached, after which it decreases rapidly. This limiting concentration is probably that at which the induction period approaches 45 hours under the conditions of the IP test.

These sludge plus acid figures, together with those obtained on the commercial oils (Table III), were plotted against the useful life periods of the oils as determined by the basic static test (graph not shown). The points were found to be widely scattered throughout the whole of an area bounded on two sides by the axes and on the third by an asymptotic curve. This curve approached the useful life period axis at a value of about 50 hours, and began to run parallel with the sludge–acid axis at about 15 hours, *i.e.* as the useful life period decreased the scatter of the IP results increased. (At 50 hours useful life period the IP results ranged from 0 to 0·5 per cent, at 15 hours from 0·2 to 1·5 per cent.) These results justify the assumptions made during the authors' early examinations of commercial oils that oils giving an IP sludge of less than 0·1 per cent had been efficiently inhibited, whereas those giving greater values were of questionable merit. This statement, of course, depends on the acceptance of the basic static test as a true measure of the comparative efficiency of inhibited oils.

(d) *Assessment of the Condition of Used Oils*

As methods in common use for the assessment of the degree of oxidative deterioration of used uninhibited oils are not wholly suitable for inhibited oils, the possibility of employing the static test for this purpose was considered. For blends which show a proportionality between induction period and inhibitor concentration the induction period can be used as a measure of the condition of a used oil. It will indicate when an oil contains sufficient inhibitor to warrant its continued use and, when the induction period of the original oil is known, the ratio of the induction periods of the new and used oils will enable some estimate to be made of the service life remaining in the oil. The use of the induction period in this manner does not apply, however, to blends with negligible induction periods, or to those with induction periods independe nt of inhibitor concentration, or to those containing antioxidants which behave as oxidation retarders and produce no induction period.

The employment of the useful life period as a criterion of the condition of a used oil is not subject to

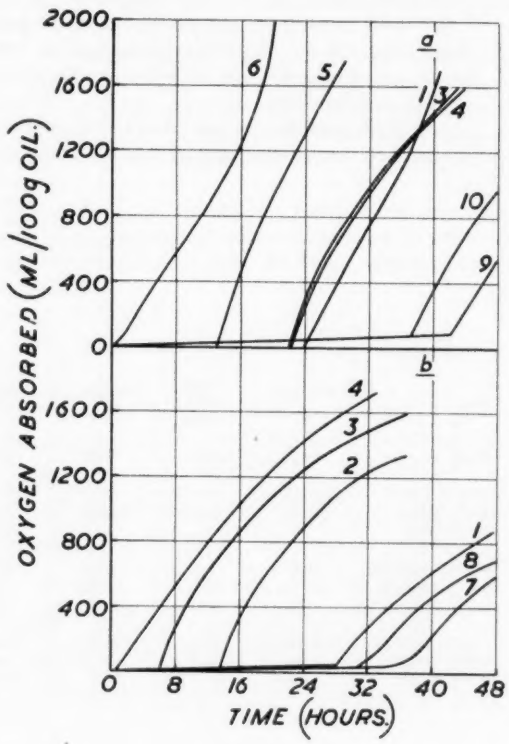

FIG 22

OXYGEN ABSORPTION OF ARTIFICIALLY AGED OILS

Oil *Y*—120° C—100 p.p.m. soluble copper

FIG 22 (*a*)

Curve No.	Description	Hours pre-aged	Acid value
1	0·25% PBN blend	0	0·02
3	0·25% PBN blend	144	0·02
4	0·25% PBN blend	216	0·04
5	0·25% PBN blend	336	0·09
6	0·25% PBN blend	504	0·12
9	No. 5 + 0·25% PBN	—	—
10	No. 6 + 0·25% PBN	—	—

FIG 22 (*b*)

Curve No.	Description	Hours pre-aged	Acid value
1	0·25% DBPC blend	0	0·02
2	0·25% DBPC blend	48	0·02
3	0·25% DBPC blend	144	0·03
4	0·25% DBPC blend	216	0·05
7	No. 2 + 0·25% DBPC	—	—
8	No. 3 + 0·25% DBPC	—	—

these limitations, and this period can be applied to all the foregoing types of anti-oxidant-containing oils.

Some experiments were made to illustrate the behaviour of used oils in the static test. Oil *Y* was blended with 0·25 per cent PBN and with 0·25 per cent DBPC, and the two blends so prepared were oxidized for several periods in the IEC oxidation equipment (in the presence of metallic copper) to produce artificially aged oils. The oxygen absorption curves of these aged oils were then determined by the basic static test.

Fig 22 shows that the useful life period of the oils progressively decreases as the artificial pre-aging period of the oils increases. It is believed that these results establish the suitability of the useful life period, as determined by the basic static test, as a means for assessing the condition of used inhibited oils and their suitability for continued use.

(e) *The Effect of Inhibitor Replenishment*

The possibility of extending the service life of a used oil by introducing additional inhibitor is a matter of practical interest. The artificially aged oils prepared for the experiments concerning the assessment of used oils formed a convenient starting point to explore experimentally this possibility. To several of these oils additional quantities of 0·25 per cent of inhibitor were added and their absorption characteristics then determined. Fig 22 shows that this addition more than restores the oils to their original condition, *i.e.* in all cases the useful life periods of the oils with 0·25 per cent additional inhibitor are greater than those of the original unaged oils. This is not difficult to understand for used oils in which some inhibitor still remains, on the assumption that the total inhibitor concentration of the replenished oils is then greater than 0·25 per cent, but the result is unexpected in oil 5, Fig 22 (*a*), for this oil had been pre-aged to the stage at which all the original inhibitor had apparently been used up, and yet the replenished oil gave a result indicating that the concentration was greater than 0·25 per cent. The explanation apparently is that there must still have been some inhibitor remaining in solution which became active when the additional 0·25 per cent was introduced.

These results are of importance in proving that inhibitor replenishment of a used oil is a practical proposition, and that an oil can be restored to its original condition as regards oxidation stability by the addition of more inhibitor.

The practical value of this conclusion may be limited by the general contamination to which an oil is subjected during long periods in service and which may affect other properties, such as electric strength, but this is a matter which can be decided by an appropriate examination before a used oil is considered for inhibitor replenishment.

(f) *The Behaviour of Oils Containing Two Inhibitors*

There is a risk that under service conditions a transformer may be filled with two or even more oils containing different inhibitors. This may be either accidental or intentional. It is, for example, possible that a transformer filled originally with one oil may be topped up at a later date with another oil, or that during the original fill-up two oils were available and used indiscriminately. The behaviour of mixed inhibitors was therefore explored, the experiments being limited to mixtures of two inhibitors. Three blends of oil *X* were prepared, each containing 0·25 per cent of one of the inhibitors PBN, 24M6B, and DBPC. These blends were then mixed to give three more samples, each containing equal proportions of two inhibitors, *i.e.* one containing 0·125 per cent PBN plus 0·125 per cent 24M6B, the second similar percentages of PBN and DBPC, and the third similar percentages of

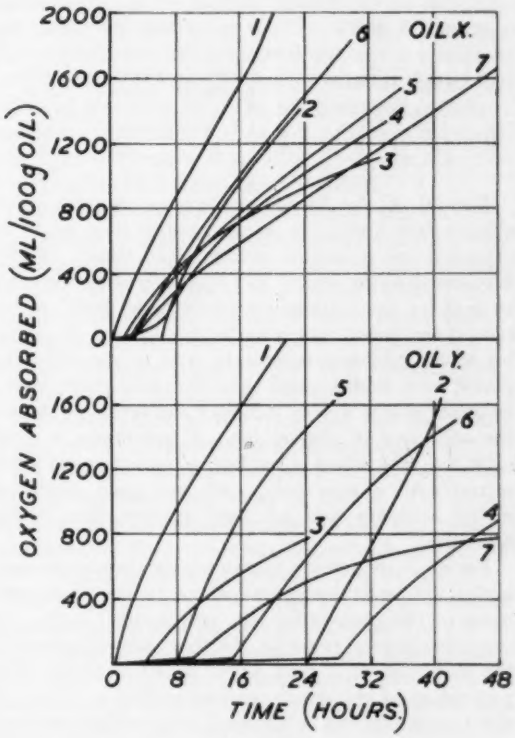

FIG 23

OXYGEN ABSORPTION OF OILS WITH MIXED INHIBITORS

120° C—100 p.p.m. soluble copper

Curve No. 1—B.S. 148 oil
Curve No. 2—0·25% PBN blend
Curve No. 3—0·25% 24M6B blend
Curve No. 4—0·25% DBPC blend
Curve No. 5—0·125% PBN + 0·125% 24M6B
Curve No. 6—0·125% PBN + 0·125% DBPC
Curve No. 7—0·125% 24M6B + 0·125% DBPC

24M6B and DBPC. This procedure was repeated with oil *Y*.

Basic static absorption tests were made on these samples (Fig 23). Comparison will be facilitated by the following tabulation of the useful life period:

Oil	Useful life period, hours					
	0·25%			0·125% + 0·125%		
	PBN	24M6B	DBPC	PBN + 24M6B	PBN + DBPC	24M6B + DBPC
X	8	5	9	7	6	8
Y	27	9	33	10	19	17

For oil *Y* the blends containing two inhibitors always gave useful life periods shorter than might be expected on a simple arithmetical basis. In the first example the period was approximately the same as that for the more feeble inhibitor by itself, in the second the period was considerably shorter than that for either inhibitor separately, and in the third the period was slightly less than the arithmetic mean. In other words, a poor inhibitor can seriously impair the efficiency of a good one, or conversely, a good inhibitor may effect a negligible improvement when mixed with a poor one; and two good inhibitors mixed together can be less efficient than either separately.

For oil *X* the blends containing two inhibitors gave useful life periods approximating to the arithmetic mean of the periods for the constituent blends. As the experimental error for the short periods given by the blends of oil *X* may have formed an appreciable proportion of the whole, and as inefficient blends of this type would not be accepted in industrial practice, it is considered that the conclusions relating to oil *Y* are the ones of practical importance.

The post-useful life periods are not in a region of direct interest to the oil user and have not been compared in detail, but it is interesting to note that oil *Y* with mixed 24M6B and DBPC has a longer post-useful life period than any of the other blends. This behaviour is also present with oil *X*, although it is not so pronounced.

The general conclusion from these experiments is that it is bad practice to mix inhibited oils.

(2) *Characteristics of Commercial Oils*

(a) *Transformer Oils*

The majority of inhibited transformer oils commercially available about 1955 were examined for their oxidation characteristics. Oils *A* to *G* are inhibited oils available in the U.K., one of them containing a passivator. Oil *H* is an inhibited oil conforming to U.S. practice. Oil *X* is a typical B.S. 148 uninhibited oil included for the purpose of reference.

These oils were examined by all the methods previously described and, in addition, by IP 56 modified to use 100 p.p.m. of soluble copper in place of metallic copper. The oxygen absorption curves for these oils are given in Figs 24–26. The numerical results appear in Table III and also in Fig 27, in which

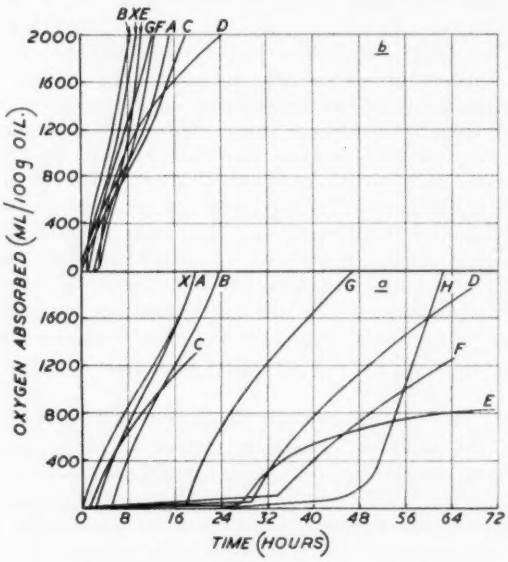

FIG 24

OXYGEN ABSORPTION OF COMMERCIAL INHIBITED TRANSFORMER OILS

(*a*) 120° C
(*b*) 150° C—100 p.p.m. soluble copper

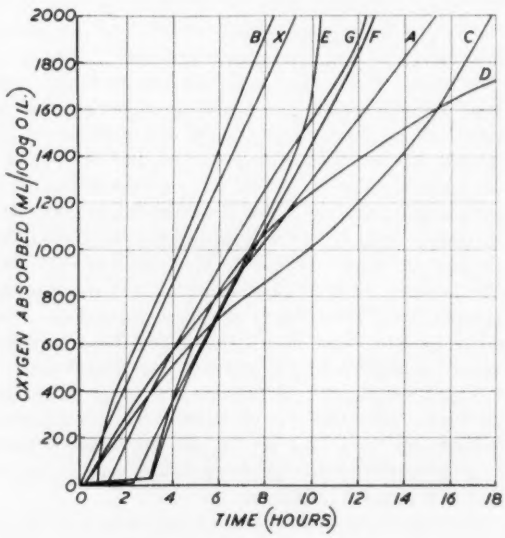

FIG 25

FIG 24 (*b*) ON LARGER SCALE

they are arranged in quantitative order of merit. The following observations are based on these results.

The oils differ widely in their oxidation stability as assessed by the different methods of test.

Their relative order of merit (rating) differs with the method used. (i) The ratings as assessed by IP 56 sludge, acidity, and sludge plus acidity results and by the useful life periods with soluble copper at 120° and 150° C, are in agreement except for minor transpositions. (ii) The rating by the useful life period with metallic copper at 150° C differs from the rating common to the tests in (i). (iii) The ratings for the post-useful life periods with soluble copper at 120° C, with soluble copper at 150° C, and with metallic copper at 150° C, differ from each other and from those under (i) and (ii). It is suggested that the ratings given by the tests (i) and (ii) are the ones of practical importance.

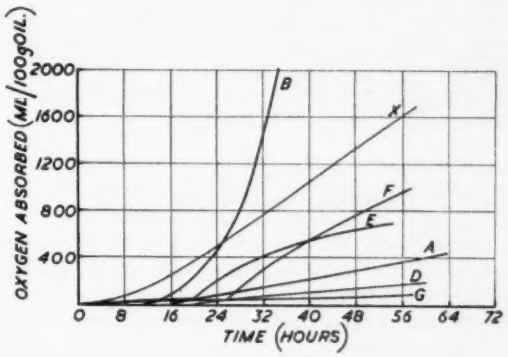

FIG 26

OXYGEN ABSORPTION OF COMMERCIAL INHIBITED TRANSFORMER OILS

150° C—5 sq. cm. metallic copper

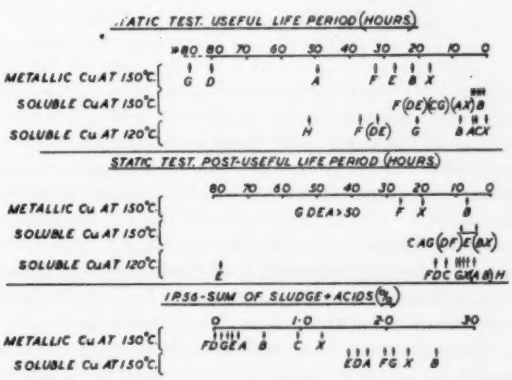
STATIC TEST. USEFUL LIFE PERIOD (HOURS)
METALLIC Cu AT 150°C
SOLUBLE Cu AT 150°C
SOLUBLE Cu AT 120°C
STATIC TEST. POST-USEFUL LIFE PERIOD (HOURS)
METALLIC Cu AT 150°C
SOLUBLE Cu AT 150°C
SOLUBLE Cu AT 120°C
IP56-SUM OF SLUDGE+ACIDS (%)
METALLIC Cu AT 150°C
SOLUBLE Cu AT 150°C

FIG 27

RESULTS OF OXIDATION TESTS ON COMMERCIAL INHIBITED TRANSFORMER OILS

Points of especial interest in the ratings table (Fig 27) are that oil *D* lies consistently near the top and the uninhibited oil *X* consistently near the bottom for all test methods; and that the useful life period of oil *G* with metallic copper at 150° C and the post-useful life period of oil *E* with soluble copper at 120° C are outstandingly superior to those of the other oils.

None of the U.K. oils has a post-useful life period less than that of the typical uninhibited oil *X*. The post-useful life period for the U.S. oil *H* is less than that of oil *X*, but as its base oil was not available it was not possible to decide whether this was due to the nature of the base oil or to some adverse influence exerted by the inhibitor. As U.S. oils are often made from lighter fractions than most European oils, the former explanation seems the more likely.

In the static test with soluble copper the oils tend to approach a common performance at 150° C, but short induction periods are still present which fall into the same relative order as that found at 120° C (see Fig 25 which repeats Fig 24 (*b*) on a larger scale). This appears to indicate that the same mechanism of inhibitor depletion is operating at both temperatures, but is greatly accelerated at 150° C.

The mean value of the range for the useful life periods of the commercial oils determined at 120° C in the presence of soluble copper is ten times greater than the corresponding mean at 150° C. The mean for these oils with metallic copper at 150° C is twenty times greater than the mean for soluble copper at 150° C and twice that for soluble copper at 120° C.

The mean value of the range for the post-useful life period of the commercial oils determined at 120° C in the presence of soluble copper is eight times greater than that at 150° C. A similar comparison with metallic copper is not possible, as the post-useful life period in this case was beyond an experimentally convenient test duration.

The IP 56 sludge results of many of the oils are less than 0·1 per cent, which, according to the tentative limit suggested, indicates a satisfactory degree of inhibition. Others are not so satisfactory, but in no instance does the IP result for an inhibited oil exceed that of the base oil, an anomaly which was observed for some earlier commercial oils. The results of the modified IP test using soluble copper are in every case greater than the standard IP results for the same oil, but with one exception they are less than the results for the typical uninhibited oil *X*. The oils with the lowest sludges by IP 56 show the greatest increase when the metal is replaced by soluble copper.

In general, the commercial oils are very similar to the laboratory-blended oils in their behaviour and in the range of results given.

An experimental transformer oil containing an anti-oxidant was recently submitted by an oil supplier. This has been examined and, although it is too late to include the results in the appropriate graphs and

tables, they are of such interest that they warrant a special comment, and are as follows:

	Useful life period, hours
Static test—120° C—100 p.p.m. soluble copper	580 *
Static test—150° C—100 p.p.m. soluble copper	49
Static test—150° C—metallic copper . .	60

* By extrapolation.

This oil takes the soluble copper response at both 120° and 150° C into an entirely new range compared with the 1955 oils (Fig 27), and it is the first inhibited transformer oil examined showing approximately equal response to both metallic and soluble copper.

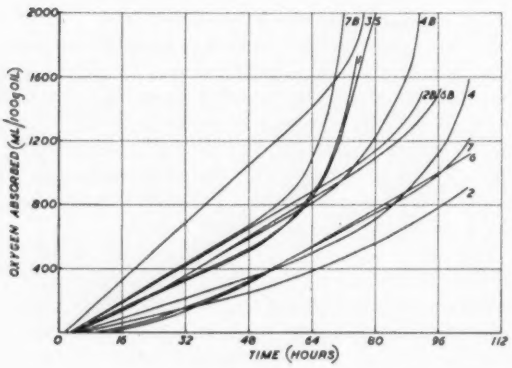

FIG 28

OXYGEN ABSORPTION OF TURBINE OILS

150° C—100 p.p.m. soluble copper (see Table IV)

IP 56 tests in the standard form and in the modified form using 100 p.p.m. of soluble copper were also made:

	Sludge, %	Acid value, mg/g
IP 56 metallic copper . .	0·03	0·06
IP 56 100 p.p.m. soluble copper .	0·07	0·1

These results confirm that the soluble copper response is approximately the same as the metallic copper response, and they differ from all previous IP 56 results in this respect.

(b) *Turbine Oils*

The successful behaviour of the static test with transformer oils suggested that it might be a suitable means for examining the oxidation stability of inhibited turbine oils. Preliminary experiments showed that the oxygen absorption of this type of oil at 120° C was negligible, but that at 150° C, using 100 p.p.m. of soluble copper, the results fell within a convenient range. Several commercial inhibited oils and, in some cases, their base oils, were examined by the static test under the above conditions, and also by IP 56. The results (Fig 28) show that the oxygen absorptions with soluble copper are of the same order as those for transformer oils at 120° C with soluble copper or at 150° C with metallic copper, *i.e.* turbine oils are very much more resistant to oxidation than transformer oils. The useful life periods of the limited number of oils examined cover a wide range, the least being 15 hours and the greatest 56 hours. As only two suppliers' oils were examined, it may well be that a wider survey of commercial oils would disclose still greater variations.

The useful life periods of the base oils lie closely grouped together around a mean value of 27 hours. Those of the inhibited oils produced from these base oils are similarly grouped together around a mean value of 48 hours. The base oils appear to be particularly stable oils when their mean useful life of 27 hours is compared with that of 15 hours given by an inhibited oil from another supplier.

TABLE IV

IP 56 Tests on Inhibited Turbine Oils

Oil		IP 56		IP 56 modified 100 p.p.m. sol. copper	
Code No. Fig 28	Description	Sludge, %	Acid value, mg/g	Sludge, %	Acid value, mg/g
1	Inhibited—light grade	0·01	0·7	—	—
2	Inhibited—light grade	0·01	0·11	0·002	Nil
2B	Base oil for No. 2	0·15	0·25	0·07	0·3
3	Inhibited—medium grade	0·05	0·5	0·02	0·6
4	Inhibited—medium grade	<0·01	0·11	0·01	0·1
4B	Base oil for No. 4	0·07	0·08	—	—
5	Inhibited—medium-heavy grade	0·01	0·4	0·03	0·6
6	Inhibited—medium-heavy grade	<0·01	0·17	0·01	0·2
6B	Base oil for No. 6	0·04	0·03	—	—
7	Inhibited—heavy grade	0·01	0·17	0·01	0·2
7B	Base oil for No. 7	0·03	Nil	—	—

The IP 56 tests on these oils (Table IV) afford excellent confirmation of the relation found for transformer oils that oils with good oxidation stability as measured by the static test yield IP 56 results of less than 0·1 per cent sludge. The IP 56 test modified to use soluble copper gives results similar in several cases to the metallic copper results, *i.e.* these oils resemble the experimental transformer oil containing anti-oxidant in that they are equally resistant to both forms of catalyst under these test conditions.

This examination of turbine oils is brief and incomplete. It is intended only to show the applicability of the static test to turbine oils, to establish suitable test conditions, and to give examples showing the order and range of the results to be expected.

CONCLUSIONS

(1) *Methods of Test*

There is not yet any commonly accepted method for evaluating inhibited transformer oils, but during these investigations the authors have become increasingly convinced of the value of the static absorp-

tion test, in agreement with the opinion of its originators.[2, 3] The reasons which emerged during the present work in favour of this view are as follows:

Of the materials commonly present in a transformer the most active oxidation catalysts are metallic copper and dissolved copper.[9] A test with either of these as catalyst can be of reasonable duration and is likely to simulate severe conditions of service.

It is preferable that an oxidation test should measure the time taken to reach the degree of oxidation at which the oil is normally taken out of service, not the degree of deterioration at a fixed time, which may put the oils in a different order of merit.

An oxidation test to be practicable must accelerate the rate of oxidation, but it is desirable that its results should be capable of correlation with service conditions and service life.

The static absorption test meets these requirements and also gives a continuous time record of the degree of oxidation for each set of conditions.

The IP 56 test, the only alternative method explored by the authors, proved useful in the early work as a means of dividing inhibited oils into two classes, one likely to give good performance, and the other of uncertain merit, but it suffers from many disadvantages. It does not correspond to operational conditions of access of oxygen, for the oil is subject to the passage of air bubbles and is rapidly circulated; it continues the oxidation to a stage far beyond that likely to be encountered in service; and the fixed time limit does not permit comparisons at the early stages of oxidation encountered in transformers. Nor is IP 56 well adapted for exploring the effect of changing variables, which sometimes demonstrate that the order of preference suggested by one set of test conditions is inverted when the conditions more nearly approximate those of service. For these reasons the static absorption test is greatly to be preferred.

As oils differ considerably in their response to metallic copper and to dissolved copper, at the concentration used in the present work, and as either or both these materials may be present in a transformer, any evaluation should take account of both these forms, and a mixed catalyst test might be considered desirable. A test temperature of 120° C, however, is impracticable for metallic copper and one of 150° C is impracticable for soluble copper. Hence satisfactory assessment requires two separate tests, one with metallic copper at 150° C and the other with soluble copper at 120° C. The most suitable soluble copper concentration is 50 p.p.m., for at this value the useful life periods of the oils are indicative of their relative susceptibility to the much smaller copper concentrations met under service conditions. An area of 5 sq. cm. of copper foil is tentatively suggested for the metal catalyst test, but as the influence of copper area has not been explored in the present work this recommendation may need modification when further data are available.

The static test apparatus can be considerably simplified for routine work if the useful life period only, as defined here, or some similar period is to be measured. The electrolytic cell and the recording instrument can be eliminated and the apparatus resolved into an oxidation flask connected to a mercury-filled manometer capable of delivering a measured 15 ml of oxygen from the sealed limb to the flask. Electrical contacts suitably arranged in the manometer can be connected to an electric clock which can be started at the beginning of the test and stopped automatically when 15 ml of oxygen (*i.e.* 300 ml O_2 per 100 g oil) has been absorbed, thereby giving a direct reading of the useful life period. This simple equipment would maintain a small positive pressure of oxygen which would not correspond with the atmospheric pressure conditions in the fully recording equipment, but this would probably not involve any great difference in the results. Equipment of this type has been described by Ward.[10]

In addition to its applicability to inhibited oils, the static test has proved of value in studying uninhibited oils at various temperatures and catalyst concentrations. In its simplified form it offers a possible supplementary method to IP 56 as a means of routine control. Modern oils are refined to give a practical compromise between sludge and acidity and differ little one from another in the ratio of these two products of oxidation. For oils complying with B.S. 148 the oxygen absorption is therefore a measure of quality, and the useful life period could be used as a measure of consistency or even for comparing oils. The advantages to be gained are shorter duration of test, greater ease of manipulation, and probably better repeatability. To give a useful life period of suitable test duration it would be necessary to choose low temperatures and low catalyst concentrations. As a result, the test would correspond more closely to operating conditions than IP 56, and it might therefore prove to be a better index of the operating performance of an oil than that test, providing that the requirement of the sludge–acidity relationship was observed. It is not impossible to determine these products in the oil at the end of the experiment, but the small quantity of sludge presents manipulative difficulties.

(2) *Base Oils*

The four B.S. oils chosen for examination differ remarkably little one from another in their absorption characteristics in the basic static test. With reduced concentrations of soluble catalyst at 120° C and with metallic copper at 150° C some differences between the oils develop. Induction periods are present at 80° C, but not at 100° C and above.

The oils respond to inhibition to varying degrees. In the basic static test the increasing order of response to all inhibitors as assessed by the useful life period is *Z*, *X*, *W*, and *Y*. This relative order is substantially maintained throughout the ranges of inhibitor concentration, temperature, and catalyst concentration explored except for a marked improvement in the position of oil *Z* at 100° C. The general trend of the temperature and catalyst concentration curves suggests, however, that below 100° C and below 50 p.p.m. of soluble copper, some significant changes in relative order and in the magnitude of the differences between oils will develop.

In the presence of metallic copper at 150° C oils *W* and *Y* respond well to all inhibitors, but oil *X* has a small response to 24M6B, and PBN and shows an increased rate of oxidation with DBPC.

(3) *Inhibitors*

In the presence of 100 p.p.m. of soluble copper, PBN produces oils with absorption curves possessing induction periods dependent on, and post-useful life periods independent of, inhibitor concentration. 24M6B produces curves with very short induction periods independent of, and post-useful life periods dependent on, inhibitor concentration. DBPC yields curves of mixed characteristics depending on the nature of the base oil. For all the oils examined the useful life period is approximately proportional to inhibitor concentration within the limits economically feasible.

The inhibitor response outlined above applies only to the basic static test conditions, and modifications may occur as a result of changes in temperature and catalyst concentration.

(4) *Temperature*

For the basic static test conditions the plots of temperature against useful life period are asymptotic. Above the knee of each curve the useful life period does not change very greatly, but below the knee it increases rapidly with decrease in temperature. The temperature at the knee varies with the nature of the oil and inhibitor. For the base oils the mean temperature is about 85° C and individual oils differ little from this mean. For the inhibited oils the mean temperature is about 115° C and the values for particular blends range from 110° to 125° C. This is a matter of practical importance, for it shows that for a given life a well-chosen inhibited oil can be operated at a temperature about 40° C greater than an uninhibited oil.

The influence of temperature on post-useful life period is also very great. The curves are again asymptotic, the knees varying from 110° C for the base oils to 120° C for some inhibited oils. For each class of oils the spread of the results is small.

Induction periods are also influenced by temperature. All the oils develop an induction period when the temperature is sufficiently reduced, and the temperature at which this period first appears is a function of the oil and inhibitor. For the base oils the temperature is about 80° C, whereas all inhibited oils still possess an induction period at 150° C. The rate of increase of the duration of the induction period varies with individual blends.

The major importance of the temperature experiments is to show the great increase in service life which occurs below a critical temperature, and the substantial increases which can be achieved both in service life and operating temperature by the matching of oil and inhibitor. Further work at lower temperatures, although very time-consuming, appears to be justified in order to confirm the trends established by extrapolation. This is also necessary because some of the curves cross each other. There is a reasonable hope that by this further work a correlation between useful life period and service life could be established.

(5) *Catalysts*

For the basic static test conditions the induction period is independent of catalyst concentration.

The plots of useful life and post-useful life periods against catalyst concentration are asymptotic. The knee for useful life period occurs at concentrations ranging from about 20 to about 60 p.p.m. and for the post-useful life period from 20 to 120 p.p.m. Maximum catalytic activity, as measured by the useful life periods of all oils, and the post-useful life periods of the base and PBN oils is reached at 100 p.p.m. For the post-useful life periods of 24M6B and DBPC blends, maximum activity is not reached until about 200 p.p.m. Below the knee both periods increase rapidly with decreasing catalyst concentration, so that at concentrations likely to be present in transformers these periods will be very long and the differences between the service life of oils may be great.

The post-useful life periods of some inhibited oils increase less rapidly with decreasing catalyst concentration than those of their base oils. As a result, their rates of oxidation after the inhibitor has been used up may, if the catalyst concentration is sufficiently reduced, approach or even exceed those of the base oils. The effect, however, is not universal, and other blends maintain the superiority of the inhibited oil over that of the base oil throughout the whole of the absorption range and catalyst concentrations explored.

The use of high concentrations of dissolved copper in the static test swamps differences in the useful life periods of the oils which have been shown to exist at lower concentrations, and the highest concentration giving results in a reasonable test period while still

differentiating between the likely response of the oils at operating concentrations is 50 p.p.m.

Under the test conditions used in this work and for the majority of oils examined, metallic copper is a far less active catalyst than soluble copper, the order of oxygen absorption for metallic copper at 150° C corresponding very approximately with that for soluble copper at 120° C. Oils do not respond in the same relative order to metallic and soluble copper in the amounts used. Some appear to be far more resistant to metallic copper than to soluble copper, and vice versa. If this behaviour is repeated under the catalyst conditions existing in transformers (a possibility which needs additional work at low catalyst values to substantiate), then it should be recognized in choosing oil. A new transformer containing no varnished coils should be filled with copper-resistant oils. A new transformer containing varnish-impregnated coils, or an old transformer containing acid oil in the windings, should be filled (or refilled) with an oil resistant to soluble copper. The best procedure, however, is to choose for all cases an oil high in the merit scale for both forms of copper, and the use of the static absorption test will assist in the development and choice of such an oil.

(6) *Condition of Used Oil*

As the useful life period of an inhibited oil is approximately proportional to inhibitor concentration, this period may be used as a measure of the condition of a used oil. A single measurement indicates the presence or absence of inhibitor, and therefore the suitability of the oil for continued service; if the useful life period of the original oil is also known, the proportions of inhibitor used to that remaining can be calculated; and if the change in useful life period occurring over any period in service is known, the service life remaining in an oil can be roughly forecast, assuming that the transformer is to continue in service under the same conditions.

It must be emphasized that the forecasting of the remaining service life of an oil solely by the above means can be only a very rough approximation. Other factors enter into this problem, and have been referred to by Stoker and Thompson in a comprehensive survey of inhibited transformer oils.[11]

(7) *Replenishment of Inhibitor*

A used inhibited oil which has reached the end of its induction period as a result of inhibitor depletion can be restored to its original condition as regards oxidation stability by the addition of more of the original inhibitor. The practical importance of this procedure may be limited by other factors, such as the general contamination of an oil which occurs during long periods in service.

(8) *Mixed Inhibitors*

The mixing of oils containing different inhibitors is not good practice. For a given oil two efficient inhibitors may lose in efficiency when mixed, and a poor inhibitor may gain negligibly in efficiency when mixed with a good inhibitor. The mixing of different oils and different inhibitors has not been investigated, but the practice introduces additional complications, and should be avoided.

(9) *Commercial Oils*

The commercial inhibited transformer oils current in 1955 show a wide range in their test characteristics. In comparison with the uniformity of the uninhibited oils produced to comply with B.S. 148 this appears to indicate that at that time the development of inhibited oils was in a state of flux.

An experimental inhibited oil from an oil supplier has recently been examined which possesses outstanding temperature resistance and an extremely long useful life period in the presence of soluble copper. Its resistance to metallic copper is, however, no better than that of some of the 1955 oils. In spite of this limitation, this oil appears to foreshadow the development of commercial transformer oils of a completely different order of merit from those in the 1955 classification. The authors have consistently maintained that the primary objective of inhibitor development should be to increase the oxidation stability of oils at temperatures higher than those at present accepted as feasible, and the evidence of this new experimental oil that this objective is technically possible is encouraging.

The commercial turbine oils examined also varied greatly in their oxidation stability as assessed by the static test. In this field the most noteworthy feature was that some recently developed base oils were more oxidation stable than some earlier grades of inhibited oil. This appears to indicate that further improvements in the refining of petroleum for oxidation stability are still technically and economically feasible, but as these improved base oils are improved still further by the addition of inhibitors, the possibility of improvement in base oils does not detract from the importance of the continued study of the subject of anti-oxidants.

In conclusion, it is believed that the static absorption test is the most suitable method for studying inhibited (and possibly uninhibited) oils, and is capable of giving information not obtainable by other oxidation methods.

ACKNOWLEDGMENTS

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ELECTRICAL MEASURING TECHNIQUES AND THEIR APPLICATION TO INSULATING OILS*

By G. E. BENNETT†

SUMMARY

Electrical measurements are used for the quality control of insulating oil. The importance and significance of such tests are outlined. Apparatus for this application is described, testing techniques considered, and the electrical properties of oil discussed. Further applications of electrical measurements to oils are dealt with briefly.

INTRODUCTION

PETROLEUM oil has been used as an insulating medium in electrical equipment ever since the earliest days of power engineering. Transformers and switchgear were commonly filled with oil long before the turn of the century, and the use of petroleum in this direction ante-dated its application to paper-insulated power cables by some few years. It is probable that quality control tests of an empirical nature were initiated at the very outset; but engineers have found it necessary to incorporate more stringent and searching tests with the passage of time as the advancement of their knowledge has led to a better understanding of the characteristics which are desirable and necessary in insulating oils. The stimulus to the engineer to find improved materials and to test them more rigorously has come from both commercial and technical considerations. Dielectrics of improved quality permit reduced thicknesses of insulation, resulting in an economy of raw materials in production and more efficient operation of the equipment in service. From the technical aspect, it is certain that the transmission voltages at present in use and envisaged for the future could never be achieved without vast improvement upon the dielectric characteristics of the early insulating materials and, in particular, those of the insulating oils. Each major step towards higher operating voltages has had its attendant technical problems, bringing to light the deficiencies and limitations of the materials in use at the time, and resulting in new tests being devised to assess the suitability of the modified insulants.

The problems associated with sampling of electrical oil are not discussed in the present paper. However, the avoidance of contamination in sampling insulating oils is of paramount importance, and the IP has already given specific attention to the subject in the handbook of Standard Methods under reference IP 51.

ELECTRIC STRENGTH TEST

The measurement of electric strength was probably the earliest electrical test to be applied to insulating oil. Although the electric strength may be determined using alternating or continuous voltages, or uni-directional impulses of either positive or negative polarity, it is the instantaneous breakdown value under a.c. conditions to which reference is most frequently made. The present paper does not attempt a detailed discussion of this aspect of electric strength measurement because it is currently the subject of a revival of work internationally and is, therefore, in a state of flux.

A.c. Breakdown

The basic requirement of this test is that an alternating voltage of good sinusoidal wave form should be applied between two electrodes immersed in a vessel of oil and increased until a sustained arc is formed between the electrodes. It is not at all

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apparent to the layman that a test with these seemingly simple requirements is, in fact, fraught with difficulties. A measurement of this type is incorporated as a routine test in all national specifications for transformer and switch oils. That the electric strength of even new insulating oil as determined by the conventional methods of routine test is in no way an indication of the intrinsic electric strength of pure hydrocarbon oil itself, but is profoundly influenced by the extent to which the oil is contaminated with fibres and moisture, was established as long ago as 1917 by Hirobe, working in the Electrotechnical Laboratory at Tokyo. This, together with the fact that the electric strength test has gained for itself a reputation of extreme unreliability owing to its dependence upon highly controversial factors, has caused it to be regarded with disfavour in many quarters, and it is, in any case, a very unsatisfactory criterion of the condition of an oil which has been in service. However, the test will undoubtedly be retained, despite its many shortcomings, simply because no other measurement has yet been devised which is as simple to perform in the field and will provide the same information. To measure accurately the degree of contamination of oil with moisture and fibres is a long and tedious process even under carefully controlled laboratory conditions, and would be impossible in the field.

Electric strength apparatus and, in particular, oil test cells, differ in design quite considerably from one country to another. For example, spherical electrodes of approximately 13 mm diameter are used in the U.K., France, Sweden, and Switzerland, but in the U.S.A. flat disk electrodes of 1 inch diameter with square cut edges are employed, and in Germany mushroom shaped electrodes having an effective radius of 25 mm are specified. The electrode design has an important bearing upon the measured electric strength of a sample of insulating oil, the reason being that the contaminants most usually present in oil migrate towards the zone of highest stress. In the case of spherical electrodes, this zone is the shortest distance between the spheres, whereas with disk electrodes the greatest stress concentration is at the edges, and thus the contaminating fibres are distributed over a wider area. In the case of the German-designed electrodes, the field distribution is more uniform than in the other cases mentioned, and therefore the concentration of contaminants is not so marked. It is, of course, a debatable point whether it is desirable to concentrate the contaminants in one point and so make the conditions of test the most severe possible, or whether the contaminants should be left uniformly distributed throughout the stressed zone of the sample and so an average electric strength obtained.

The test gap specified by different nations also varies considerably, ranging from 2 mm to 5 mm. Further variations between national specifications are introduced in the method of applying the voltage. There are two schools of thought on the subject, one which considers that the voltage should be raised steadily until breakdown occurs, and the other which considers it desirable that the oil should withstand a specified voltage for a given period of time. The first school of thought is supported by the U.S.A., Belgium, and Germany, while, on the other hand, the British National Standard [1] requires the sample to withstand the test voltage for a period of 1 minute, the Italian (using 10-mm spheres) for a period of 5 minutes, and the Swiss for a period of 30 minutes. Again, the French national specification requires that the sample shall withstand the applied voltage for 1 minute at each of several specified levels as the stress is being increased. In such circumstances it is difficult to compare the pass levels of electric strength of the specifications of different countries. The wide divergence of test procedures can be illustrated by comparing the methods of the U.S.A. and Switzerland, the former requiring an instantaneous breakdown stress of approximately 100 kV/cm, while the latter requires a withstand stress of 60 kV/cm for 30 minutes. General dissatisfaction among experts and doubts as to the usefulness of electric strength tests caused a committee of the Conférence Internationale des Grandes Réseaux Électriques à Haute Tension to hold a special meeting in London, in April 1955, to discuss the subject, as a result of which it has become one for study internationally by the International Electrotechnical Commission.

There are yet further factors to be considered which affect the breakdown strength of oil. The specification requirement for new oil is not applicable to oil which has been in service in electrical equipment, since oxidation of oil produces sludge and organic acids which impair its electric strength; but the test is a most unreliable guide to the serviceability of oil, and there are many instances of oil having high acid value and satisfactory electric strength.

A possible alternative to the breakdown test which gives a better indication of the future serviceability of transformer oil has been suggested by Forrest,[2] which involves a resistivity measurement, and this test will be considered later.

We have considered so far in a general way only how the design of the electrodes and application of the test voltage may influence the breakdown test. Attention must also be paid to the design of the testing transformer. It has already been noted that the output should have a good sinusoidal wave form. This is important from the point of view of standardization, but there is also a reason of deeper significance. An insulant which is tested to breakdown using an a.c. supply will fail in the first instance at a voltage peak. The voltage most commonly referred to when considering an alternating supply is the " root mean square " (r.m.s.) voltage, which has a fixed relation

to the peak voltage, as given by the expression $V_{peak} = \sqrt{2} \times V$ r.m.s. for sinusoidal qualities. It is possible for an alternating voltage of non-sinusoidal wave form to have an r.m.s. value equivalent to one with a sinusoidal wave form, but a peak value greatly in excess of $\sqrt{2}$ times the r.m.s. value.

Furthermore, the impedance of the test set should not be too high, or the arc may not be sustained through the oil at breakdown, in which case the test will not discriminate between breakdown and a transient sparking. Whether or not transient sparking should be regarded as failure is a still further point of controversy between experts.

Appreciating the fact that the a.c. electric strength test is one in which a wide random scatter of results must be expected, it has been suggested by a committee, which has investigated the test in the current British Standard,[1] that the procedure be retained in its present form, but that borderline cases should be assessed having regard to an analysis which is more justified by statistical considerations than the present method, according to which the oil passes if two out of three samples meet the requirements of the specification. A summary of the position has been made by Stoker and has been published as a report,[3] which tabulates the electric strength procedures for eight countries. References of other recent publications concerned with this subject are given at the end of the paper.[4–8]

Since the a.c. electric strength test is profoundly influenced by the presence of moist fibres, which are destroyed by the arc when breakdown occurs, repeat tests are not possible on one filling of the oil cell. On the other hand, the random scatter of results makes a statistical approach desirable, and it would obviously be a great advantage to carry out a large number of tests in rapid sequence on any one given filling of oil.

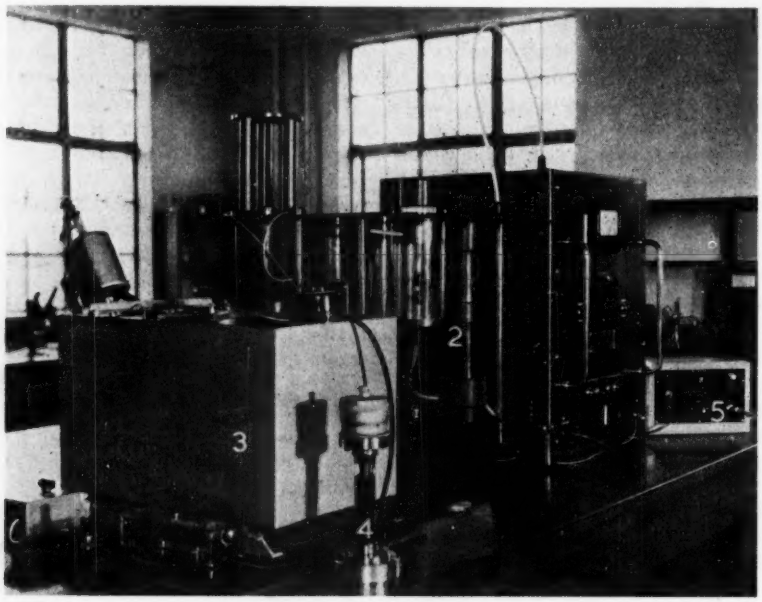


FIG 1

IMPULSE TESTING APPARATUS

1. 60-kV d.c. set
2. Single-stage impulse generator
3. Thermostatically controlled oil bath
4. Test cell
5. Electronic breakdown detector

Solutions to the problem have been sought by Watson and Higham [9] and also by Baker.[10] Their investigations have been directed towards extinguishing the arc within a very few micro-seconds of its being formed, thus avoiding the destruction of any constituent of the oil or contaminants therein. The efficacy of their methods is proved by the fact that up to several thousand tests may be performed on one filling without any evidence of the formation of carbon and comparatively little increase in apparent electric strength.

Impulse Breakdown

A very considerable amount of laboratory work has been done in recent years on the electric strength of oil using uni-directional impulses. Lightning strokes on overhead lines and switching surges in

high voltage circuits give rise to transient over-voltages on the associated cable, and the ability of the cable to withstand such conditions is, for the highest voltage cable, a limiting factor in design. Some experts are of the opinion that the impulse strength of an oil-impregnated paper cable is influenced by,[11] or even primarily dependent upon,[12] the impulse strength of the saturant in the butt spaces adjacent to the conductor. In Europe, it is usual to test cables using a nominally 1/50 voltage wave, that is to say, the voltage rises to its maximum in approximately

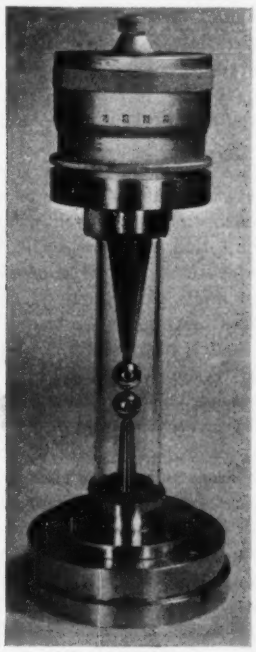


FIG 2
IMPULSE BREAKDOWN TEST CELL

1 micro-second and decays thereafter to half maximum voltage in 50 micro-seconds. When testing oil, it has been found that if the duration of the wave tail is reduced, the electric strength increases. This effect is very pronounced in the first few micro-seconds, but thereafter the effect is diminished. The advantage of reducing the length of the wave tail lies in the fact that damage to the testing electrodes by pitting is reduced, and repeated tests on one sample are possible owing to the very limited formation of carbon at breakdown. In the author's laboratories considerable work has been done on the impulse strength of oil using a 1/5 impulse wave and a test gap of 5 mils (0·005 inch), which is of the order of that found in the butt spaces of cable dielectric. For this work an impulse generator having an output voltage of 50 kV is adequate, which may easily be achieved from a single-stage set (see Fig 1), thus avoiding the complications of design of a multi-stage generator. The setting of a test gap of such small dimensions is extremely critical, and a test cell of the type described in B.S. 148 for the routine testing of transformer oil under a.c. conditions is quite unsuitable. Special test cells with high sensitivity micrometer adjustments are essential (see Fig 2). Although the impulse electric strength of insulating oil appears to be less influenced by contaminants than are tests under a.c. conditions, the scatter of test results is nevertheless considerable, and any investigation has to be approached on a statistical basis, necessitating a large number of tests on one sample of oil.

Other investigators [13] have pursued their researches employing a circuit which applies rectangular pulses to the oil under investigation.

D.c. Breakdown

In view of the increased interest in the possibilities of high voltage d.c. transmission, the investigation of insulating oil under steady d.c. voltages is important, and much work has already been done on the subject by Zein el Dine and Tropper.[14]

DIELECTRIC LOSS ANGLE OR POWER FACTOR

While the measurement of a.c. breakdown is probably the electrical test most widely applied to insulating oil, it will have been realized that, owing to its shortcomings, it is not the most informative. The measurement of power factor of insulating oil is the most useful single test which can be applied to determine its qualities as a dielectric, particularly with reference to power cables and capacitors.

A short explanation of the term "power factor" will be inserted here, as the author has noted definitions in published literature [15] which clearly show there is confusion of thought on the subject. In an electric circuit, the power factor is that factor by which the apparent power, the product of volts and amperes, has to be multiplied in order to determine the actual power of the circuit in watts. Considering the particular case when a sinusoidal voltage is applied to a perfect capacitor, the charging current pulsations lead those of the applied voltage by 90° (see Fig 3): that is to say, the current is at its maximum value when the voltage is zero, and this time displacement of the current and voltage waves remains constant as long as there is no external influence upon the circuit. The information imparted by Fig 3 may be expressed more simply by means of a vector diagram (see Fig 4 (*a*)), in which the electrical quantities involved in the circuit in both time and magnitude are represented by vectors. A perfect

capacitor has a power consumption of zero, hence it follows that the power factor of a perfect capacitor is zero. In practice, owing to the fact that dielectrics are imperfect, a relatively small amount of power is dissipated in the capacitor, and the angle by which the current vector falls short of 90° is known as the dielectric loss angle (see Fig 4 (*b*)). Since the values we have to consider are small, the dielectric loss angle in circular measure (D.L.A.) is, for all practical purposes, numerically equal to the tangent of the dielectric loss angle, and also equals the cosine of the

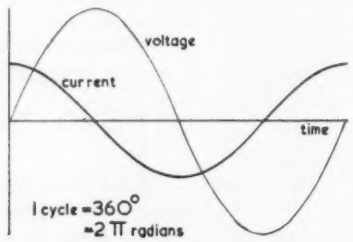


FIG 3
GRAPHIC REPRESENTATION OF CURRENT AND VOLTAGE FOR A PERFECT CAPACITOR

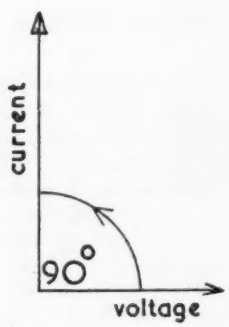
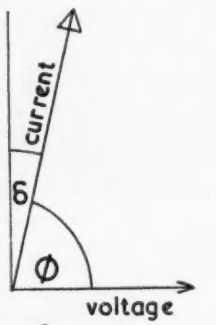


FIG 4 (*a*)
VECTOR DIAGRAM FOR PERFECT CAPACITOR



δ^c = D.L.A.

Φ = phase angle

FIG 4 (*b*)
VECTOR DIAGRAM FOR IMPERFECT CAPACITOR

phase angle, which is the power factor. In order to avoid confusion of thought with the power engineer, who would usually regard a power factor of unity as desirable, transmission and capacitor engineers frequently adopt the term "dielectric loss angle" in preference to power factor. For small values (say, less than 0·05) "power factor" and "dissipation factor," which latter term is also used in this connexion, are equivalent.

From the foregoing remarks, it will be seen that the energy dissipated in the dielectric is proportional to the dielectric loss angle, and, apart from adding to the running costs of the equipment, appears as an additional heat loss. A high D.L.A. may lead to thermal instability in the case of combined oil and paper dielectric, since the D.L.A. of, *inter alia*, paper/oil dielectrics rises at temperatures above that of normal operation, causing, in turn, further temperature rise, and ultimate failure of the insulant.

Present-day super voltage electric power cables (*i.e.* cables designed for 33 kV and over) have D.L.A. values commonly between 0·002 and 0·003 at ambient temperature, which values show an improvement of approximately 100 times over those of early power cables.[16] This enormous improvement is due in no small measure to the improvement in quality of insulating compounds and oil used in their manufacture.

Because of their high value, the early measurements of this characteristic could be made using watt-meter methods of measurement. Alternatively, an electrical bridge circuit due to Wien could be employed. As dielectrics and insulating oil improved and values of dielectric loss angle were achieved below a level of about 0·01, these methods were found to be too insensitive. In 1920 a bridge circuit was suggested by Schering[17] for the measurement of dielectric loss angle at high voltage. This circuit proved to be both very sensitive and versatile, and undoubtedly made a large contribution to the technical advances in dielectrics which have been achieved since that time. The original basic circuit incorporated a fixed standard capacitor, and ratio arms embodying a variable capacitor and a variable resistance. A modification frequently introduced for oil testing is to employ a variable standard capacitor in place of the fixed capacitor, thus permitting fixed resistances in the ratio arms. This modification is possible on account of the limited range of test capacitance when measuring insulating oil. Present-day oil test cells, when filled, generally have capacitance values between 50 and 500 micro-micro-farads.

When measuring very low values of dielectric loss angle on samples of small capacitance, attention must be paid to the effects of stray capacitance on the readings. The Wagner earthing system is a means whereby these stray effects are reduced virtually to zero and has been used in conjunction with the Schering network from the outset. It involves the introduction of two additional arms into the circuit, across the bridge supply, their junction point being earthed (see Fig 5). None of the four points of the basic bridge circuit is earthed, but the detector may be connected between the bridge points, or alternatively switched to one bridge point and the earth point. This modification has the disadvantage that at least three balance operations are necessary to obtain a reading. Investigators [18–21] in this field have

designed alternative means of surmounting the problem of stray capacitance. In a bridge with so limited an application, it is possible to design the circuit in such a way that the stray capacitance values are self-cancelling or may be allowed for by a very simple arithmetical correction.

International agreement on the technique of measurement of dielectric loss angle of insulating oil has been one of the main preoccupations of a CIGRE committee [22] since the second world war. The early work of this committee and the co-operating laboratories (which include some in the U.K.) showed in a most striking way the extreme divergence which could be obtained on these measurements. As a result, the enquiry was pursued in two directions.

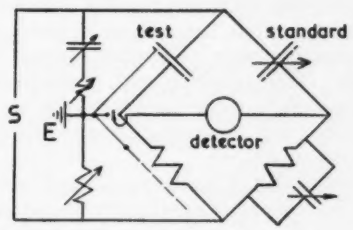


FIG 5

CIRCUIT DIAGRAM OF SCHERING BRIDGE FOR OIL TESTING, INCORPORATING WAGNER EARTH

S = current supply at desired frequency

First, artificial power factor units, which had arbitrary but constant values of dielectric loss angle, were circulated between the participating laboratories. The resultant measurements on these units made in many different countries all over the world using bridge circuits embodying many variations showed that, provided reasonable care and attention was given to the design and construction of the bridge, a truly remarkable degree of agreement could be achieved.

The second part of the investigation was concentrated upon test cells and their design and construction. Although dielectric loss angle is theoretically a characteristic of the medium under test and independent of the geometry or construction of the test cell, considerable evidence was produced to show that the design of test cells did, in fact, influence the measurements made on insulating oil. The work of this committee is still progressing, and a sub-committee has been formed whose energies are directed towards the design and construction of an oil test cell which will have international approval.

The design of a suitable test cell creates an interesting problem which has received the attention of many investigators. Briefly, a two-terminal test cell offers the advantages of extreme simplicity and lends itself to ease of cleaning and rapid testing, and is therefore most suitable for routine measurements. On the other hand, a three-terminal test cell, incorporating a guard system, is unquestionably more desirable from a theoretical standpoint and is preferred by most investigators for precision testing and research work. Further points which have to be considered are the choice of suitable materials for the cell insulators, the choice of metal for the test cell construction and the decision whether or not to use a test cell having plated metal surfaces, and, if so, what metal should be used for this purpose. Among the metals which have been used for test cell construction are stainless steel, brass, and invar, and for plating, chromium, nickel, and rhodium. The general consensus of opinion is towards a three-terminal unplated cell of stainless steel construction, with ideally quartz or, alternatively, glass insulators, which preferably should not be below the level of the oil surface.

Test cells of small physical dimensions are to be preferred, facilitating handling and rapid temperature stabilization. The effective electrode length is commonly between 5 and 10 cm, and the overall length of cell about 15 cm. A test gap of 1 mm is frequently employed, and the oil volume of cells can be as little as 15 ml.

In order that the earth capacitance of the low voltage terminal may be reduced to a negligible value, or alternatively be kept at a constant value, it is the usual practice to use the outer casing of the test cell as the high voltage electrode. Stray capacitance from the high tension side of the cell to earth merely shunts the bridge supply and does not affect the balance position.

Two typical test cells, one a two-terminal design and the other a three-terminal design, are shown in Figs 6 and 7.

Present-day insulating oils which have been properly refined are almost entirely free from polar (*i.e.* non-hydrocarbon) molecules and have dielectric loss angle characteristics of an extremely low order. For the manufacture of paper-insulated power cables and power capacitors, additives are often blended with the base oil, and the two most commonly used in all countries of the world are rosin, also known as colophony, which is a naturally occurring resin obtained from pine trees and consists mainly of abietic acid, and poly*iso*butylene, usually of a low or intermediate molecular weight. Poly*iso*butylene does not materially influence the dielectric loss angle characteristic of insulating oil; but the addition of rosin to insulating oil has an interesting effect, its molecule being of a polar structure. Fig 8 shows the influence of temperature upon dielectric loss angle for both insulating oil and rosin compound. Dielectric loss angle is, furthermore, frequency-dependent, and the effect of increasing frequency is to displace the entire curve pattern along the abscissa to the right.

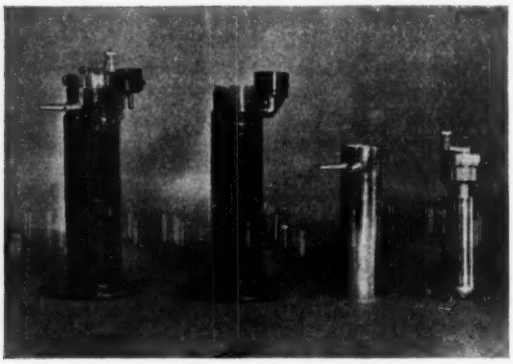


FIG 6

TWO-TERMINAL OIL TEST CELL (N.P.L. DESIGN)

Oil volume approx 16 ml; empty capacitance approx 90 micro-micro-farads.
(*Left to right*) Cell assembled in electric heating jacket; heating jacket; cell components.

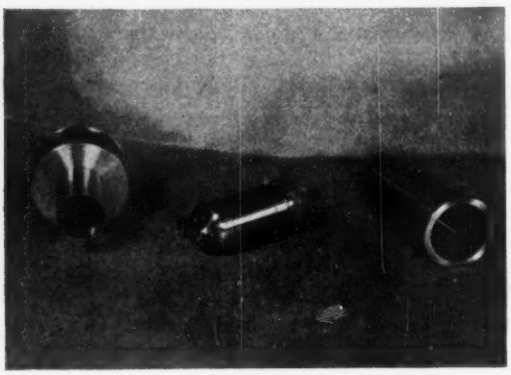


FIG 7

THREE-TERMINAL OIL TEST CELL (BRAMLEY DESIGN [19])

Oil volume approx 70 ml; empty capacitance approx 50 micro-micro-farads.
(*Left to right*) Terminal screens; inner (low tension) electrode with guard rings; outer (high tension) electrode.

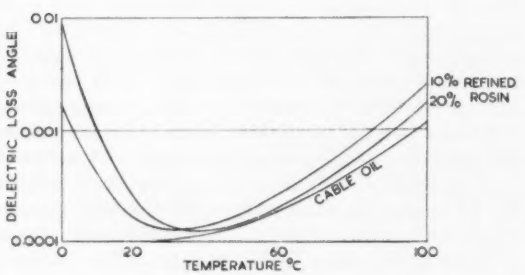


FIG 8

D.L.A./TEMPERATURE CHARACTERISTICS OF CABLE OIL AND ROSIN COMPOUND

(D.L.A. at 50 c.p.s.)

PERMITTIVITY

The permittivity, otherwise known as dielectric constant or specific inductive capacity, of insulating oil is an important characteristic, but one that is not influenced greatly by refining technique. It is true that the presence of polar molecules in insulating oil will increase its permittivity, but the characteristic is very insensitive in this direction. The permittivity of oil is important in that it influences the capacitance of the composite dielectric, paper impregnated with oil, which is widely used for electrical insulation. At ambient temperature the value of permittivity for insulating oil is commonly between 2·1 and 2·3, and the addition of 20 per cent of rosin raises the value to approximately 2·5. The characteristic is temperature-dependent and related to specific gravity, falling in an approximately linear relationship with an increase in temperature; but the change is small over the normal operating range of temperatures of electrical equipment. This relatively flat characteristic is a great advantage in capacitor design, the capacitance of the finished unit remaining almost constant under all operating conditions.

The permittivity of insulating oil may be measured using the same apparatus as that for the determination of dielectric loss angle. The capacitance of the empty test cell may be measured directly, or arrived at by calculation if the geometry of the test cell is simple, from which the permittivity of the oil may be deduced. Any capacitance bridge will suffice to make the measurement, but the Schering bridge, being essential in laboratories engaged upon the investigation of electrical properties of insulating oils, is usually readily available.

RESISTIVITY

Prior to the measurement of dielectric loss angle, the measurement of d.c. resistivity was used to assess the quality and suitability of insulating oils, particularly for power cable manufacture. Since that time, the importance attached to resistivity has diminished, because the measurement of dielectric loss angle takes into consideration both polar and conductivity effects. An oil could have a good resistivity characteristic, but be an unsuitable saturant for an oil/paper dielectric owing to the presence of polar components which would be revealed only by the measurement of D.L.A. It will be apparent that, for oil which is free of polar components, a relationship will exist between D.L.A. (at a given frequency) and resistivity (see Appendix I), provided that both measurements are made at the same temperature, and this fact can be of value in investigations on oil contamination and deterioration. Thus, if D.L.A. and resistivity measurements are made on an oil sample at two temperatures sufficiently different and it is found that the value of the product

of the two varies, then this is an indication that the electrical losses in the oil are not to be ascribed to conductance (*i.e.* non-polar components) alone.

To-day, resistivity is considered only as a useful supplementary test for oil quality and is often dispensed with altogether, although it is not by any means regarded as obsolete. The traditional method of measuring resistivity, using a high sensitivity galvanometer in conjunction with a universal shunt, remains to-day the most sensitive and accurate means at a technician's disposal. High-class apparatus of this type can measure accurately a resistance of 10^{12} ohms, which enables a measurement to be made, when using a suitable test cell, on insulating oil having a resistivity as high as 10^{15} ohms/cm^3.

Test cells which are suitable for the measurement of dielectric loss angle or permittivity are, in general, suitable also for the measurement of d.c. resistivity, which may be determined by multiplying the measured resistance of the oil dielectric by the cell constant. The cell constant may easily be calculated if the configuration of the electrodes is simple, *e.g.* when a parallel plate system is used or a concentric cylinder design; but if, as is usually the case, the geometry of the active electrodes is complex, it is very convenient to determine the cell constant by measuring its capacitance in air in micro-micro-farads and multiplying this value by a factor of 11·3.[2] When measuring both D.L.A. and resistivity on the same sample it is advisable to do the tests in that sequence, to avoid any possible "clean up" effect on polar impurities by the action of the direct current.

Resistivity is a characteristic of insulating oil which is highly temperature-dependent and follows an approximately logarithmic law, as does the viscosity, decreasing in value with increasing temperature. At ambient temperature, the value for present-day insulating oil is so high that it is beyond the range of sensitivity even of the above-mentioned galvanometer equipment. For this reason, measurements are usually carried out at elevated temperature, and frequently a temperature of 60° C is adopted.

A galvanometer is too delicate an instrument to be used except under laboratory conditions, and in recent years robust electronic instruments have been developed for the measurement of a very high resistance. These instruments apply a very highly stabilized d.c. potential to the sample under investigation, and the current which flows through the sample is magnified by means of a d.c. amplifier of great stability. The amplified output current operates a precision edgewise moving coil meter, the reading of which is a reciprocal function of the resistance under test. The accuracy of such instruments is poor compared with the galvanometer system when measurements are made at their extreme range, but highly satisfactory for values of resistance up to 10^{11} ohms. Electronic instruments of greater sensitivity are being developed which should be at least as sensitive and accurate as the conventional galvanometer.

Resistivity measurements may be applied to the assessment of the condition of transformer oil in service in a manner described by Forrest.[2] The resistivity/temperature characteristics of transformer oils considered good, passable, and poor have been determined and arbitrary limits fixed based upon this data, so that a spot test at any temperature can, by reference to a chart, indicate whether or not the oil in the transformer is fit for further service. Owing to the fact that oil from a transformer which has been in service for some time may be appreciably contaminated with sludge and other mechanical impurities, small laboratory type test cells of the type described

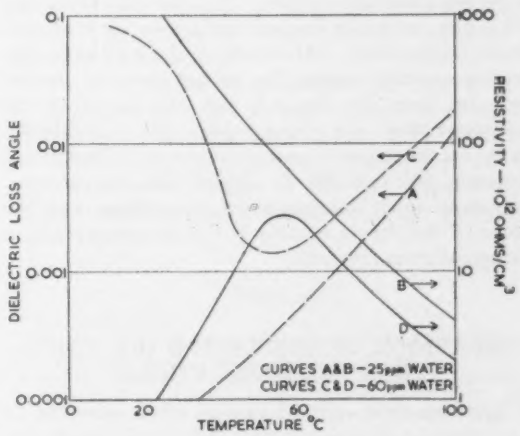


FIG 9

EFFECT OF MOISTURE CONTENT ON ELECTRICAL CHARACTERISTICS OF INSULATING OIL

(D.L.A. at 50 c.p.s.)

earlier are not suitable for this application. A special test cell has been devised, having more generous spacing between the high voltage and low voltage electrodes, so that the test gap cannot be bridged by any ordinary contaminants. The use of a larger test gap necessitates the use of a higher test voltage, and 5 kV is normally applied to a sample. Any instrument which is capable of measuring resistance in a range 10^2 to 10^5 megohms at the required voltage may be used in conjunction with this test cell. An ohmmeter of the electronic type, incorporating a 5-kV d.c. supply, is particularly suitable. The current through the oil is measured by means of a cathode-ray indicator tube. The resistance is read off directly from a dial after noting the shadow angle of the magic eye.

Resistivity measurements on insulating oil are particularly sensitive to the presence of free moisture. Dissolved moisture appears in general to have rela-

tively little, but nevertheless quite measurable, influence upon electrical measurements, but suspended moisture, present even in very small quantities measured in parts per million, can have a profound effect upon the resistivity of insulating oil. The solubility of water in oil increases as temperature increases. Oil which may be apparently of good quality and free from moisture when tested at elevated temperature may, on cooling to ambient temperature, give resistivity characteristics of a very low order, even though the amount of water present is too small to be detected visibly or by means of the well-known "crackle" test. Fig 9 shows characteristics of a typical cable oil. The sample having a water content of 25 p.p.m. may be regarded as dry by commercial standards, and its appearance at ambient temperature was clear and bright. The same oil containing 60 p.p.m. of water showed slight cloudiness at ambient temperature. Above 60° C the oil having the higher moisture content has poorer electrical characteristics than the dry oil, but the slopes of the characteristics are comparable. The equilibrium point for the moisture content of the wet oil is reached between 50° and 60° C. Below this temperature, moisture slowly condenses out of solution, and the slope of the curves relating D.L.A. (or resistivity) to temperature is reversed.

BEHAVIOUR OF INSULATING OIL UNDER HIGH ELECTRIC STRESS

The behaviour of insulating oil when subjected to high electric stress is clearly a matter of primary importance. That solid waxy deterioration products might be formed in oil under such conditions was well known to engineers in the 1920s, but it was in 1933 that the problem was brought sharply into focus in the U.K. Unexpected troubles were experienced after the first installations of "oil-filled" (or "hollow core") cables, which led to a thorough investigation of the subject. It is now well known that oils, particularly those with a primarily paraffinic structure, may evolve gas under electric stress. The gas, which is principally hydrogen, will form pockets within the cable dielectric and ionize. The high velocity ions, impinging upon the adjacent cellulose and oil components of the dielectric, cause deterioration resulting possibly in failure. It is for this reason that cable and capacitor oils are preferred which are naphthenic in character and contain a sufficient proportion of aromatic constituents to ensure that overall there is no evolution of gas under any normal conditions of stress or temperature. Research workers, having established the desirability of using oils having an absorption characteristic, designed apparatus to investigate the subject further and to carry out control tests on oil consignments. Experiments have been carried out under different gaseous atmospheres and also *in vacuo*.[23–30] The principle of the test is to apply a high voltage between two electrodes, which are usually arranged concentrically, across the oil under investigation, a gas space which contains a percentage of oil vapour being left above the oil. Sometimes cable paper is incorporated in the test as well.[25, 29] The source of voltage is from an a.c. supply, which should have a good sinusoidal wave form. This characteristic of insulating oil is stress-dependent above a certain critical inception level, below which gassing phenomena do not occur. A picture of the apparatus adopted by many laboratories in the U.K. as a referee test is shown in Fig 10: the procedure for this test has been described.[31]

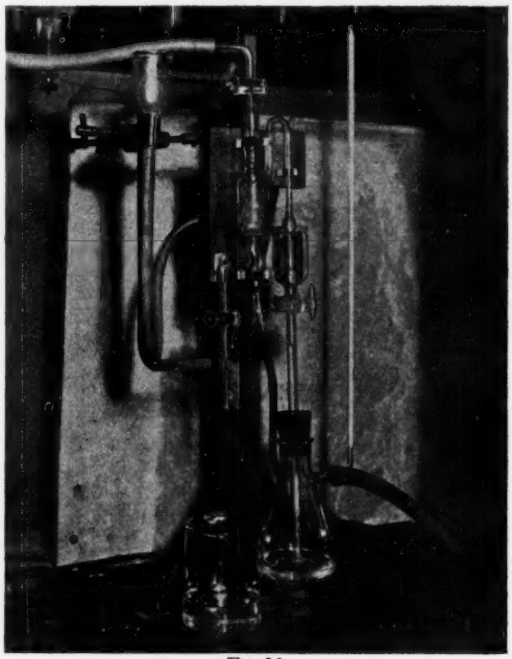


FIG 10

APPARATUS FOR INVESTIGATION OF GASSING CHARACTERISTICS OF INSULATING OIL SUBJECTED TO HIGH ELECTRIC STRESS [31]

FURTHER APPLICATIONS OF ELECTRICAL MEASURING TECHNIQUES TO INSULATING OILS

Moisture is well known to be the arch enemy of electrical insulation, and the cause of a failure in electrical equipment can very frequently be traced to the ingress of water. The detection of moisture in insulating oil, and also in insulation impregnated with oil, is therefore of very considerable importance. It

has already been mentioned that the presence of free water influences the commonly applied tests of electric strength, dielectric loss angle, and resistivity, but the detection of moisture by these means is only qualitative. A method of applying a.c. bridge technique to the quantitative estimation of moisture in oil is the subject of a report by Rushall.[32] Briefly, the test involves measuring the change in dielectric loss angle of a filter-paper, through which has been passed a known volume of the oil under test. It is essential that the filter-paper is maintained in a perfectly dry state until the very moment before the oil is passed through the paper. In order that electrical measurements may be made, the filter-paper is held clamped between perforated metal electrodes throughout the test. The change in dielectric loss angle of the filter-paper may be used as a measure of the water content of the oil. It will be appreciated that this method of measurement is a straightforward application of the Schering bridge network. It is not yet known whether the method may be applied to any but new insulating oil, since used oil, particularly that drawn from transformers, will in general contain the products of ageing, including organic acids, which might well invalidate the readings.

An alternative bridge method which may be applied to the above measurement has been described by Mole.[33] If the test piece under investigation takes the form of a capacitor, it has been found that the variation of shunt capacitance with frequency is a sensitive measure of moisture content. In this bridge network, capacitance measurements are made at two frequencies, one usually being chosen at 50 cycles per second and the other at 0·5 cycles per second, and adjustments are made to the bridge arms so that the voltages across two particular branches of the network are in quadrature, that is to say, there is an electrical phase displacement between them of 90°. This equipment is too elaborate for routine testing, and the measurement may more conveniently be made by means of an instrument called the dispersion meter.[33] This is an electronic instrument which gives a direct measurement of a characteristic known as dielectric dispersion, and consists essentially of two circuits which generate pulses of rectangular wave form and having durations of 300 and 3 milliseconds respectively. The specimen is charged electrically by the application of the 300-millisecond pulse, which is followed immediately by a 3-millisecond short-circuiting pulse, and is then isolated. It will normally develop a recovery voltage which may be measured by means of a suitable valve voltmeter. The dispersion is defined as $D = \frac{V_1}{V_0 - V_1}$, where V_0 is the charging voltage and V_1 is the peak recovery voltage. An estimated moisture content of about 0·1 per cent may be determined on impregnated paper using this instrument.

CONCLUSIONS

The basic electrical measurements on insulating oils of dielectric loss angle, resistivity, permittivity, and electric strength have stood insulating oil technologists in good stead for very many years, and will undoubtedly continue to be of great importance in the future. Measurements of electric strength and dielectric loss angle have, in particular, been criticized for their lack of repeatability. The work of the CIGRE Oil Study Committee has, however, shown in the case of the measurement of dielectric loss angle that, provided sufficient care and attention is paid, discrepancies may be reduced by a factor of several times. There still remains much work to be done in this direction.

The measurement of the a.c. electric strength on oil for routine purposes is, in spite of its variability, valuable, providing the investigator or technician is aware of its limitations.

The tests devised to investigate the behaviour of insulating oil subjected to high voltage are examples of the way in which new methods have to be developed to contend with new problems. Undoubtedly, there will be further instances of this as ever-increasing voltages make greater demands upon the quality of electrical insulation.

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APPENDIX I

Relationship between dielectric loss angle and resistivity at a given temperature.

$$\rho = 11{\cdot}3 \times C_1 \times R_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ρ = resistivity in ohms/cm³;
C_1 = capacitance of empty test cell in micro-micro-farads;
R_1 = dielectric resistance in ohms measured under d.c. conditions.

$$\text{Also } \delta^r = \frac{10^{12}}{\omega C_2 R_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where δ^r = D.L.A. (dielectric loss angle in circular measure, *i.e.* radians);
$\omega = 2\pi f$;
f = frequency of the sinusoidal measuring voltage;
C_2 = capacitance of filled test cell in micro-micro-farads;
R_2 = equivalent shunt resistance in ohms of the imperfect capacitor.

Equations (1) and (2) may be deduced from electrical theory. In an oil free of polar molecules $R_1 = R_2$
Hence, for measurements at a frequency of 50 cycles per second

$$\delta^r = \frac{10^{12}}{27{\cdot}8\, k\rho}$$

where $k = \frac{C_2}{C_1}$ = dielectric constant of oil under test.

Assuming a typical average value of $k = 2{\cdot}25$ for cable oil

$$\rho\delta^r = 1{\cdot}6 \times 10^{10}$$

APPENDIX II

List of some Electrical Terms

The purpose of this short list is to explain and clarify some of the technical terms frequently used in connexion with the electrical testing of insulating oil. It must be emphasized that the following are not intended as formal definitions, which may be found in published literature,* but are more in the nature of comments designed to assist those who are not familiar with the terminology of this specialized field.

Terms which are merely cross-referred to another term are generally those less favoured or which are to some extent outmoded although still encountered.

Breakdown strength—see *electric strength*.

Breakdown voltage—is that voltage at which electric failure takes place between two electrodes across which a potential difference (voltage) is applied.

Capacitance—the ratio of the electric charge on a conductor to its potential (voltage) normally measured in micro-micro-farads (alternatively called picofarads).

Capacitor—a system of two electric conductors called electrodes, the geometry of which is designed to achieve relatively high values of *capacitance* within a small space.

Capacity—see *capacitance*.

Condenser—see *capacitor*.

Conductance—the reciprocal of *resistance*, measured in mhos.

Conductivity—the reciprocal of *resistivity*.

δ^r—see *dielectric loss angle*.

Dielectric—any insulating medium.

Dielectric constant—the ratio of the *capacitance* of a *capacitor*, having as dielectric the insulating medium under consideration, to the capacitance with air as dielectric. (The effect of having an insulating medium other than air, or more strictly vacuum, between the electrodes of a capacitor always leads to an increase in capacitance. The dielectric constant of vacuum is by definition unity and that of air 1·00059.)

Dielectric loss—the electrical power dissipated within the *dielectric* owing to the imperfections of practical *capacitors*; it is measured in watts.

Dielectric loss angle—in a perfect *capacitor* the charging current will lead the applied voltage by 90° (see text, Figs 3 and 4 (*a*)); but in practice, the current vector falls short of 90° (see Fig. 4 (*b*)). The angle by which the current vector falls short of 90° is the *loss angle*; it may be measured either in degrees or radians. In connexion with insulating oil it may be assumed always to be measured in radians, unless the contrary is specifically stated. It is given the designation δ or more correctly δ^r to denote its measurement in circular measure (radians).

Dielectric strength—see *electric strength*.

Dissipation factor—see *dielectric loss angle*.

Electric strength—the *breakdown voltage* expressed per unit (or standard) length of test gap, *e.g.* 100 kV/cm, etc.; for oil it will vary with electrode shape.

Electric stress—the voltage applied between two electrical conductors or electrodes, expressed per unit separation. Units of measurement are volts, kilovolts (10^3 volts), or megavolts (10^6 volts) per micron (10^{-3} mm), millimetre, centimetre, mil (10^{-3} inch), or inch.

Loss angle—see *dielectric loss angle*.

Loss factor—sometimes used loosely to denote the same as *loss angle*, but, correctly, this term should be used only for the product of loss angle and *dielectric constant*.

Loss tangent—see *tangent loss angle*.

Permittivity—may for practical purposes be regarded as synonymous with *dielectric constant*, when used in this connexion.

Phase angle—the angle by which the charging current vector leads the applied voltage in a *capacitor* (see text, Fig 4 (*b*)).

Power factor—see *dielectric loss angle*; power factor is sometimes expressed as a percentage (especially in the U.S.A.).

Resistance—in an electric circuit, measured under d.c. conditions, is given by the ratio of applied voltage to current and is measured in ohms, or more generally when insulating materials are being considered, in megohms (10^6 ohms) or million megohms (10^{12} ohms).

Resistivity—of an insulating material is the *resistance* of the material expressed in ohms, megohms, or million megohms per unit cube, usually per centimetre cube.

Root mean square (r.m.s.) value—the square root of the mean value of the squared ordinates (*i.e.* instantaneous values) of a periodic curve. The heating effect due to an alternating current is proportional to the r.m.s. value squared.

Specified dielectric resistance—see *resistivity*.

Specific inductive capacity—see *dielectric constant*.

Specific insulation resistance—see *resistivity*.

Specific resistance—see *resistivity*.

Tan δ—see *tangent loss angle*.

Tangent loss angle—the tangent of the *loss angle* measured in degrees. For small values (less than 0·05) it is for practical purposes numerically equal to the loss angle in radians.

* *E.g.* B.S. 205 : 1943. Glossary of terms used in electrical engineering.

DISCUSSION

P. W. L. Gossling: To open our discussion this evening we are to hear Dr J. S. Forrest, who is Director of the Central Electricity Research Laboratories at Leatherhead. Dr Forrest is a physicist of distinction, but in his earlier days with the old Central Electrical Board he had a great deal to do with the maintenance of insulating oil in service. He is Chairman of ERA Section E, the controlling committee for work on insulating oils and, from his activities on this and other of our committees, it is clear that he has retained a liking for this subject, although nowadays he has many more important duties.

Dr J. S. Forrest: As Chairman of the Section, and also at the Central Electricity Research Laboratories, I have been concerned with the overall programme of much of this work. As Mr Clinch said, this programme is an excellent example of good co-operative research. We have co-operation between two industries (the oil industry and the electrical industry); co-operation between oil suppliers, equipment manufacturers, and the ultimate users of both the equipment and the oil; and finally, co-operation between industrial and academic research workers. The careful organization of this co-operative work by Section E, particularly by Mr Gossling and Mr Norris' sub-committees, must have resulted in a considerable economy in research staff and cost. It has certainly resulted in economies as far as the ERA is concerned, because the industrial laboratories have carried out their part of the programme free of charge to the ERA, and I would like to thank them for this generous help.

A further important aspect of this co-operative programme is that it enables us to play a useful part in the international work of IEC and CIGRE.

As a result of the research carried out, and also of the service experience in the twelve years since the previous symposium, I feel that the present position is relatively satisfactory. Transformer oil is giving good service, and we now understand how to specify it, how to treat it in service, and how to recondition it. The introduction of inhibited transformer oils is an important technical advance. Materials generally limit plant design, but we are now in the unusual position of informing the plant manufacturer that he can have a better material, which will withstand more arduous conditions, if he wants it. It is important, however, to convince the plant manufacturer and user that the improvement shown by inhibited oils in accelerated oxidation tests will in fact be reproduced under actual service conditions, and I would be interested to hear if anyone can provide some information on this point.

I should also be interested to know to what extent inhibited oils are being used at present by the supply industry and other organizations.

With regard to electrical measurements, it was pointed out some time ago by Stannett and Childs that iron has a very marked effect in reducing the resistivity of transformer oil in service. Mr Liander has also emphasized the importance of studying the effect of iron in transformer oils. We do not yet know in what form the iron is present in the oil, or why it has such a pronounced influence on the electrical conductivity. This is a question of some importance both from practical and theoretical points of view, and I would welcome any comments on it. In any case I commend this problem to those making fundamental studies.

Mr Bennett refers to the standard power factor which was circulated internationally by the CIGRE committee, and he says that the resultant measurements showed that "a remarkable degree of agreement could be achieved." It should be pointed out, however, that the first time the standard was circulated some very large errors in measuring equipment were in fact disclosed, and the standard served a useful purpose in enabling the laboratories concerned to correct these errors.

In describing the measuring techniques, Mr Bennett does not attempt to give specification or operational limits for the various electrical quantities, such as resistivity or power factor. This is a difficult question, especially with used oil, but a few years ago an ERA panel, with representatives from the electrical and the oil industries, collated the best available information and reported it in a document (Ref. E/S4) on "Maintenance of Insulating Oils for Transformers and Switchgear." I am sure those concerned with this question will find that report of value.

E. T. Norris: I think that, so far as the present-day use of transformer oil is concerned, all this work is quite unnecessary. The oil suppliers as a whole have done a wonderful piece of work in giving the transformer engineers and the manufacturers in industry some very excellent material which, as it is being used at present, is practically perfect for its job. I think that present-day engineers, users, and manufacturers can quite forget that there ever are, or were, such phenomena as acidity and sludge.

Acidity and sludge have had some prominence in recent years, but I think that bears reflection on the oil itself, but is entirely due to contaminants, which need not and should not have been in the oil in the first place. I know of many cases where transformer oil has been in service for twenty and thirty years and it is as good now as the day it was put in.

What can we do, therefore, to make use of all the work that is in these papers? I think there are two possible suggestions. One is that maybe all this knowledge that the oil people are acquiring in the course of this work will enable them to produce oil which is as good as they are making now, but perhaps to produce it more simply and cheaply, so that the price will come down.

The second possibility, and I think this is one which should be studied more and more, is that if there is any good in this work at all and if any improvements are being made, then surely it should be possible to raise the average working temperature of the oil. That would be a very fine thing, both for the manufacturer and the user, in that it would result in cheaper transformers. I would suggest that all the people who are doing this work should bear in mind the possibility of being able to increase the temperature of oil. It is a very complex business, because the oil in any electrical apparatus is associated with a solid insulation, and in present practice, which has been evolved over many years, that combination has been very intimate indeed, and the co-ordination has been extraordinarily good. If we do find that we can put up the temperature of oil by 20° C, say, we shall then have to consider the solid insulation, which will, of course, go up 20° C correspondingly, in addition to the 20° or 30° that it is hotter than the oil anyway. Therefore I think this sort of work should be considered more in the light of making use of it by the only way I know by increasing the temperature of the oil. There may be other limits, of course. There may be the factor of

safety over the flashpoint and firepoint getting too small, but that also is one of the things that should be considered.

My last point concerns the electric strength and, as the author says, there has been a great deal of study of this. A number of competent, authoritative research teams, in the U.K. and other countries, have been measuring the electric strength in various ways, under various conditions, and all getting different results. This leads to discussions and is very perplexing. I think the matter should be looked at in this way. The general picture that we are presented with is that we have all these authoritative research teams measuring the electric strength of oil. I think that is exactly what they are not doing. What they are measuring is the effect of minute impurities. The electric strength of oil is enormous, millions of volts per inch, and no practical oil gets anywhere near it. It is these very minute impurities that are causing all this trouble.

If it is looked at in that light, and bearing in mind that none of these research teams and bodies make any attempt at all to see that they are measuring the same impurities, either in quantity or quality, is it surprising that they get different results, and would it not be simply astonishing if they happened to get exactly the same results?

L. H. Welch: Mr Norris says "let us raise the temperature limits, let us alter the insulation, let us use less copper, less material of all kinds, and get more out of the apparatus." I think everybody is basically in favour, but it is rare for advantage to be taken of the temperatures that are at present permitted. When the electricity supply industry does take advantage of these temperatures, then I shall have every sympathy with trying to raise them higher still.

However, it must be remembered that a good system has some spare plant and therefore the maximum load on an individual item of plant depends on the failure of nearby plant. This means that it is only on rare occasions that a really heavy load, with consequent high temperatures, occurs.

On many distribution systems the maximum load occurs on the coldest days, and if transformers are in the open or in well-ventilated chambers they are able to carry a load considerably above their nameplate rating before the temperature of the oil reaches even its normal value. On such systems, with maximum loads occurring for so few hours during the year, it is almost impossible to have high temperatures for long periods.

Mr Norris also said that the oil industry had done remarkably well, and there was no need to worry any more. I agree that the oil industry has done very well after a sad setback in the 1920s, but we used to think our transformers would last twenty-five years, and now we want them to last fifty years. Consequently, oil is needed that will last fifty years in transformers, with only minor maintenance. It appears the oil companies can do this, but want to charge 3*d*. or more a gallon extra. As a consumer, I see no particular reason why we should pay this extra amount.

The point has been made, quite rightly, that far too many people have thought they were testing the quality of the oil when using the dielectric strength test. This test is only useful to show whether the oil is clean and free from water or other impurities, and I think the time has come, in this industry of ours, to ask for and accept a certificate at the works that the oil is a good quality oil, and then to test on delivery that it has not been contaminated in transit. After all, it is accepted practice to accept a works certificate for switchgear, transformers, etc., so why not use the same procedure for oil? I am sure there is now no need to be worried about the constitution of the oil, as good oil is available from the suppliers, so let us get our certificate from the works, and then, when we get the oil on site, use a simple dielectric strength test to see that there are not too many bits of fibre, or anything else, in the oil.

Dr Forrest said we knew how to recondition oil. We do, but if he was referring to oil with a high acid content the only sensible method is to return it to the manufacturers for processing. He also said we used inhibited oil, but as it costs 3*d*. a gallon more, and the London Electricity Board buys a large quantity of oil annually, a straight oil is always specified and used in London, and should be satisfactory.

The ERA have excelled in their dealings with oil. As has been mentioned already, they have achieved great co-operation between many bodies, and it is fair to say that they have been favoured by having more work done at less cost to themselves in labour or money than in any other area of their research. They have endeavoured to arrive at a code of practice for the maintenance of oil and produced such a document, but unfortunately at that time it was felt that it was not right for them to issue it, and that it should be issued by the BSI. The BSI embraces the supply industry, manufacturers, consultants, and even other countries, and this inevitably leads to irritating delays, as nearly every paragraph is rewritten. That state of affairs has existed now for two years, but I sincerely hope that at the next meeting of the BSI it will be found that every objector has been satisfied, and that it will be possible to commence printing a Code of Practice for the Maintenance of Insulating Oil within three months from now.

P. W. L. Gossling: It is very important for us to obtain as much information as we can upon the trend of oil temperatures in service. I would ask if a member of the BSI Committee dealing with the transformer specification, BS 171, could tell us about the proposals for a Code of Practice.

E. Tobin: Normal operation of transformers is about eight hours a day working at high load, with comparatively low load during the night hours and early morning. Under these conditions the permissible hot spot temperature in the winding is 105° C for 8 hours and 80° C for the remaining 16 hours. Supplying a double shift load of about 16 hours a day at high load, the permissible hot spot temperature is 100° C for 16 hours, or for 24 hours constant load, such as mill motor loads, the permissible hot spot temperature is 95° C.

Under these various loading conditions the maximum oil temperature would in each case be somewhere about the same value, approximately 70° C, due largely to the long thermal time constant of an oil-immersed transformer, *i.e.* the length of time required for the materials to heat up.

The above conditions would be obtained with a cooling air temperature about 20° C and full rated load for 24 hours each day, alternatively higher than rated load for the period of double-shift or single-shift working, with considerably reduced load for the remainder of the day.

Transformers have not always been worked up to their maximum capacity; the loading has been such that the oil temperature was nearer 60° C and the oils have behaved very well.

There is a tendency to increase the loading on transformers to use as much as possible of their permissible loading.

If the oil was suitable for operating at a higher tem-

perature than formerly, it might be a valuable contribution for very large transformers that are now being required for 200–300 MVA and where transport becomes quite a problem.

We might be able to increase the working density on the materials in the transformer and thereby reduce the transport weight.

Agreed, paper insulation is also a limiting factor, but there is continual research on insulation, as well as on oils and the other materials.

There may eventually be some insulation other than paper, or even paper without oxygen access might be satisfactory at a little higher temperature.

Referring to the papers dealing with iron and copper in solution, as there is such a very small amount in solution in the oil even after a long period in service, although there is plenty of iron and copper accessible in a transformer, and it is stated that the oil will not hold big quantities in solution, would it be better to base tests or investigations on big quantities of added soluble copper and soluble iron, rather than on small quantities, so that any oil independent of its construction can take up what quantity of iron and copper it wants?

J. M. Ward: Three out of the nine papers in this symposium deal almost exclusively with studies of insulating oils containing anti-oxidants. These, together with other papers published in the U.K. during the past few years by refiners and users alike, reflect considerable interest in anti-oxidants for insulating oils and also represent a considerable advance in our knowledge of them. In this connexion it is gratifying that the papers at present under discussion give full details of the anti-oxidants and concentrations used in the experimental studies. In the past, such information has often been lacking in published papers on inhibited transformer oils.

These papers, however, represent only part of the large amount of work which is being done in the laboratory and in the field. We at Central Electricity Research Laboratories have been carrying out field trials for several years in collaboration with oil refiners and transformer manufacturers after making laboratory studies of oxygen absorption characteristics of oils inhibited with known chemical substances. Some of this laboratory work has been published by Childs.*

The objects of these trials are:

(1) to find out whether, with a given base oil, inhibitors would be rated in the same order of efficacy as in the laboratory tests;

(2) to find out, if possible, what relationship there is between the induction period in hours in a laboratory test and the induction period in years in the field test;

(3) to find out whether there are any unsuspected snags in using inhibited oil in service.

These trials are being made in sets of transformers as nearly identical as possible to enable a comparison of straight oil to be made with the same oil containing anti-oxidant. In some cases the set consists of a pair, in one instance it consists of six 36-MVA generator transformers. In all about fifty distribution transformers with capacities from 50 to 1500 kVA and ten 36-MVA generator transformers are being used—a total of nearly 400 MVA installed capacity.

Some of these trials have now been running for six years. So far the only positive answer to be obtained is that there have been no snags of any importance. Although the results show that the inhibited oils are deteriorating at a slower rate than the straight oils, there has been only a small degree of deterioration. The reason is that the oil temperature has been for the most part well below 65° C in spite of our attempts to find transformers which were working under onerous conditions. Generator transformers were chosen, for example, because these should run at full rated capacity for most of the operating year.

This brings me to my main point. As the result of a large amount of research and development, we have oils which should be considerably better than the conventional oils to BS 148 : 1951, and there is every prospect of making greater improvements. But are we able to derive any real benefits from using them? Most transformers, as made and operated at the moment, do not seem to require them. Inhibited oils can, of course, be useful when a transformer for one reason or another is running under exceptional conditions, but there are not a large number of such transformers. Inhibited oils can be used in doubtful cases to give an added factor of safety. But if full advantage were taken of them in designing a transformer, could a smaller transformer be made for a given duty? Besides offering the hope that this step would help to keep the cost of electricity down, it may also help to solve the problems arising out of the sheer size of transformers for the 275-kV system.

We hear informal opinions from transformer manufacturers on this subject from time to time. Everyone working in this field would, however, welcome an authoritative assessment of the difficulties and the possible advantages of designing transformers to run at higher temperatures.

G. O. Castell: Nobody will admit having used inhibited oil, although we transformer manufacturers have supplied a large amount in the past twelve years. We have not kept a very scientific check on these oils, but they have behaved satisfactorily in doing the job we required of them.

At the end of the war there was a number of transformers in which the oil was giving bad service. For years they had been heavily loaded in positions where blast protection and black-out precautions had impaired the ventilation, they had been consistently overheated and underserviced, and the oil was badly sludged. The transformers were cleaned and the oil changed, but owing to the impossibility of getting the coil surfaces and ducts quite free of sludge, the new oil began to deteriorate immediately.

What we then did in seven or eight cases, covering in all about thirty transformers, all working in bad conditions, was to clean down the cores and coils again and fill the transformers with inhibited oil.

In every case the inhibited oil has given good service over a period varying from eight to twelve years.

L. Massey: Mr Norris expressed the opinion that transformer oils are perfectly satisfactory in service and that in consequence the research and development work which finds expression in this symposium is unnecessary.

May I suggest that present-day oils are satisfactory because of the continued effort which has been maintained in the field by the oil companies and associated groups of workers! It is very necessary that research should be continued, not only to ensure that the oils will continue to meet present requirements with an adequate factor of safety, but also to ensure that improved oils will be available when made necessary by future engineering design. Insulating materials in general are

* Childs, D. G. *J. Inst. Petrol.*, 1955, **41**, 283.

still the materials which limit electrical engineering progress, and it must be very gratifying to the oil companies to know that their oils are not limiting engineering design. I wonder, however, whether this happy state of affairs is not partly due to the practice of operating transformers well within their rated capacity, as stated by Mr Welch. The oil in a large percentage of transformers never exceeds a temperature of about 60° C, and it is not impossible that more oil troubles would be experienced if the operating temperatures approached the limits permitted by BS 171. Certainly at these temperatures the factor of safety for the oil would be very much reduced.

P. W. L. Gossling: If there is anyone present from the distribution side of the electrical industry in the U.K. who is using inhibited oil in a large way in their transformer systems, we would be pleased to learn of their experiences.

In addition, there are the trials which are being supervised by ERA, about which perhaps Mr Romney, who is Chairman of the relevant ERA Panel, could tell us the progress.

J. Romney: Most of the papers in this symposium discuss the oxidation of oil, how it happens, and what can be done to try to stop it happening. Mr Norris has made a point in asking why we are trying so hard.

Of course, we are always trying to improve transformer oils, and the intensity of our efforts in that direction does not seem to depend on the state of the game at any particular moment. In other words, when transformer oil generally available was bad, we tried hard to improve it; now that it is pretty good, we are trying just as hard to make it even better.

However, the important question is: to what extent should we accept any improvements achieved? Obviously, we have to consider how much improvement we are to get, and how much it is to cost us in the shape of higher price and any possible disadvantages.

We want oils to last as long as possible, and the modern tendency, with a view to achieving this, is to use chemical inhibitors. I use the word " chemical " to distinguish them from the " natural " inhibitors which exist in the petroleum from which transformer oil is made. But I think it worthwhile considering how far we have got even without chemical inhibitors, and previous speakers have looked at that question. Dr Forrest says present-day oil is not too bad, providing it is treated right; Mr Welch says " this oil is good enough for me "; and Mr Norris says our transformer oil is marvellous. I should like to illustrate these statements by bringing up to date information provided in a paper presented in 1952 by Mr Gossling and Mr Welch, referring to practical trials proceeding at that time in seventeen transformers. Four oils were being used, three meeting the present BS 148 : 1951, although that specification was yet to come, since the trials started in 1943. The fourth would have been out of specification on acidity after oxidation. I am concerned only with the first three, those that meet the present specification. They have now been in the transformers for about fifteen years, and the highest acidity recorded is under 0·4 mg, while in eight cases it is still under 0·2. This is not too bad for fifteen years, and for uninhibited oils.

Now let us turn to inhibited oils. Mr Gossling has referred to trials under the auspices of the ERA and these, too, involve seventeen transformers. These tests have been going on for exactly five years, and three oils are concerned. One is an uninhibited oil meeting BS 148 : 1951, the others are inhibited oils, one containing a phenolic oxidation inhibitor and the other an amino compound. After the first couple of years the operating temperatures were deliberately raised so that we were getting top oil temperatures of 70° to 80° C.

We have been carrying out many tests on samples drawn periodically, but I want to refer only to the acidity figures, which are available for all the oils up to the four and a half years stage. For three transformers containing the uninhibited oil, the figures are 0·13, 0·06, and 0·17, with an average of 0·12. I cannot quote from memory the individual figures for the inhibited oils in the other fourteen transformers, but they range from 0·08 to 0·18, with an average of 0·13; in other words, much the same as for the inhibited oil.

I want to make one thing quite clear. When starting these trials, we made no attempt to formulate a particularly good inhibited oil in order to see whether an inhibited oil could behave better than an uninhibited one. We selected as the uninhibited oil a mixture of oils from different sources, checked that the mixture met the BS specification, and then introduced 0·25 per cent of either inhibitor. Thus there was no question of trying to match inhibitor to oil. I think it fair to point out that in two different oxidation tests which were carried out on the three oils, the inhibited oils showed up much better than the uninhibited oil. The present position is, therefore, that there is no evidence that the inhibited oils are behaving better, or that the particular oxidation tests we used correlate well with practice.

I want to stress that all this is not to be taken as an attack on inhibited oils. On the contrary, the company with which I am associated has been working just as hard as any other on this problem, and I do not mind admitting that we think we are developing something pretty remarkable. However, the information I have given does emphasize the need, already mentioned by some speakers, for a reliable oxidation test for inhibited oils which will correlate with service results. In that respect, I believe that the papers in this symposium, and in particular the IEC work in which the ERA is co-operating, will make a useful contribution.

Dr L. G. Wood: There may appear to be some discrepancies between figures quoted in Mr Thompson's paper and in ours, whereas in fact this is not so.

We both determined the amount of solid copper dissolved in transformer oils of different types, of different degrees of aromaticity.

In our case we worked under conditions where very little, if any, oxidation occurred. If one refers to Table III of our paper it will be noted that oils A, B, and C, all refined from the same base stock, had aromatic contents of 22, 12, and 1·4 per cent respectively and, under our conditions, dissolved 1·2, 0·6, and 0·05 p.p.m. of copper.

As the acidity development was in no case greater than 0·05 mg KOH/g, we assumed that no significant oxidation had occurred.

Mr Thompson finds that the solubility of copper in oils of different aromatic content varies inversely with the aromatic content, as can be seen from his Tables II and III.

Oil	Aromatics, Wt %	Copper concn p.p.m.		Acid development, mg KOH/g
		Oil	Total	
I.R.O. 3 .	5·6	2·2	5·1	21·35
I.R.O. 4 .	9·8	1·8	2·3	1·83
I.R.O. 5 .	17·9	0·6	1·5	0·17

The conditions of test in this case were 110° C for 164 hours with 1·6 times the standard IEC catalyst area present, and oxygen passing through the oil at 1 litre/hour.

Thus, Mr Thompson's experiments were carried out under strongly oxidizing conditions and ours were not.

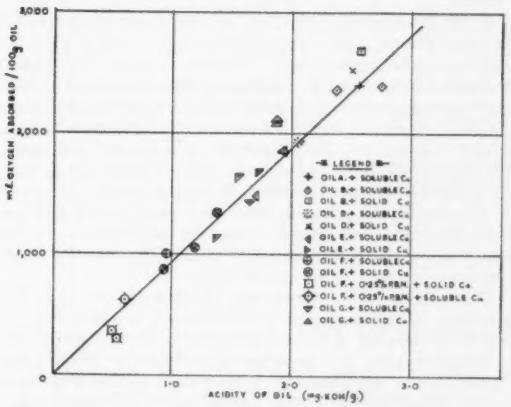

FIG D

CORRELATION BETWEEN OXYGEN ABSORBED AND ACIDITY DEVELOPMENT CIRCULATORY OXIDATION TEST

The other point I wish to make is in regard to Mr Massey's results on his static oxygen absorption apparatus.

After seeing Mr Massey's paper, we attempted to correlate the amount of oxygen absorbed per 100 g of oil in our circulatory oxygen absorption test with the acidity developed by the oil.

As can be seen (Fig D), we found that on our apparatus oils developed an acidity of 1 mg KOH/g after the absorption of just less than 1000 ml of oxygen/100 g of oil.

In our tests we used oils from different crudes and refined to different extents (oils A, B, D, E, F, and G in our paper), covering a wide range. I would therefore suggest that it would be unwise to extrapolate the results obtained on one apparatus to another, as the difference between Mr Massey's 300 ml and our 1000 ml is sufficient to make a considerable difference to the "useful life period of an oil."

E. H. Reynolds: I think it might be appropriate if I put in a general word for users of insulating oils other than transformer oils.

I am referring to those who make cables and power capacitors, whose problems are of rather a different order of magnitude. It is especially interesting to note, having listened to the excellent studies which have been made on the oxidation mechanisms of hydrocarbons, that as far as a cable or a power capacitor is concerned, if the acidity developed in the oil were to increase above 0·15 mg KOH/g one would not have electric light in one's house. In power cables we have to deal with degradation at a rather lower level, and with a mechanism which is rather difficult to study in conventional apparatus.

Therefore, we have to use rather different techniques, concerned mainly with a study of contaminants and trace compounds.

Five years ago my company started with high hopes that we would be able to produce evidence which would persuade the oil companies that they could supply us with a material more suited to our purposes, giving longer life and improved electrical properties. We have now come to the conclusion that the oil as supplied is remarkably good, and that the troubles which we experienced have largely been due to the introduction during processing, handling, and impregnation of contaminants derived from ill-chosen components or materials, *e.g.* varnished cambric tapes, cotton and rayon binders, dirty copper, and steel.

This is not to say that there are not good oils and those not so good. In this connexion I think it would be appropriate if I could refer for a moment to a "hare" that has been running in the insulating oil world for a very long time now. I am referring to the phenomenon known as "gassing."

In considering the significance of "gassing" of oils, I am referring to it in connexion with paper dielectrics which have to operate at very considerably higher electrical stresses than is customary in transformers, *i.e.* electrical stresses of the order of 60 kV/cm and upwards. It has often been asserted that in an oil/paper system, which must be hermetically sealed, the oil should not be of a character which under these orders of electrical stresses evolves any gas which may subsequently form voids leading to ionization.

With this in view, we have spent quite a lot of time in trying to answer the question: Is it essential for an oil in cables or power capacitors to be gas-absorbent? The first problem was whether we should do the test under the atmosphere of hydrogen, which has normally been the case, or whether we should seek to do it under an atmosphere which actually obtains in the equipment concerned. This would be an almost exclusive atmosphere of nitrogen, since any residual oxygen would already have been absorbed by the oil concerned. Using a standardized gassing cell, we obtained a series of curves of gas evolution/absorption against time for various insulating oils under hydrogen which very largely agreed with the curves derived by the respective manufacturers. Most oils evolved gas, some absorbed only a little gas, some oils absorbed it heavily. In those tests we also included some inhibited transformer oils, and it was also of interest to note the wide variations in gas absorption found between inhibited and normal oils from the same supplier.

However, as hydrogen is initially unlikely to be present in voids in cable or capacitor dielectrics, we made parallel tests under nitrogen. We found that every low viscosity oil tested of roughly equivalent volatility, in a standard "gassing" cell, evolved gas to a greater or lesser extent.

The major controlling factor in determining the gas evolution characteristic was the proportion of the naphthalenes in the oil. By increasing these the gas evolution tendency was decreased. At the same time, of course, the oxidation stability deteriorated, since in general those oils with a higher aromatic content tend on the whole to be more susceptible to oxidation than those with a lower proportion.

In conclusion, we cannot recommend to the oil manufacturers that they can provide us with significantly better oils than we have at the moment. The user must ensure that he does not contaminate or degrade it by contact with undesirable materials, *e.g.* oil-soluble polar materials or oxygen. Furthermore, we are inclined to doubt whether the gas evolution or absorption characteristics of an oil bear any strict relation to the performance of a paper cable or capacitor, and this view is supported by life test data on sealed power capacitors, operating at stresses up to 220 kV/cm, with the three types of oil mentioned.

A. W. Stannett: Mr Bennett's paper is interesting, not only in its own right, but also because it illustrates the different approach to transformer and cable oils. All the other papers in the symposium relate mainly to the aging of transformer oils. With cables and capacitors, however, the compound or oil does not age appreciably in service, and so advantage can be taken of the good electrical properties of the oils and high stresses used. In transformers, aging is the rule, and so the initially good electrical properties of the oil cannot be used to full advantage. It is to be hoped that the work done with inhibitors and with sealing of transformers will change this state of affairs and that economies in size of equipment will occur.

In most cases the acidity rejection limit of 1 mg KOH/g for transformer oils in service automatically rejects oils whose electrical properties are becoming dangerously poor, but the correlation between acidity and either power factor or resistivity is not complete, and cases occur where one or other of the electrical tests mentioned is needed to ensure safe operation. We find that the polar contribution to power factor is negligible at all temperatures on transformer type oils and at working temperatures (60° C or so and above) on all other commercial insulating fluids. For routine purposes, therefore, the power factor test, which requires expensive equipment, is not necessary, the d.c. resistivity test being adequate. It would be useful to hear Mr Bennett's opinion on the matter.

Referring to the CIGRE work on oil test cells mentioned in the paper, it may be of interest to note that a prototype cell has been produced. Stainless steel electrodes and quartz insulation are used. Preliminary tests on the cell, which is simpler in construction than most precision cells, are promising.

P. W. L. Gossling: Although there are several more asking to speak, we can only allow time for one more, and I would like that to be Mr Biske. This gives me an opportunity to express my thanks to Mr Biske for the great help that he has been to all concerned with the organization of this symposium. Further, although he has not contributed a paper, he has contributed quite a large amount of the work of which you have heard in two of the papers. Thank you very much, Mr Biske, for the help that you have been to me personally.

V. Biske: Some points occur to me arising from Dr Salomon's contribution to the discussion, in connexion with his view that " pure " oil will not readily oxidize. He suggested that a " contaminant," acting as an initiator of oxidation, could be present in oils that do easily oxidize and that its concentration might be of the order of 10^{-6}. Has Dr Salomon thought of using gas–liquid chromatography to try to detect what such contaminant could be? Such technique is now being applied to the investigation of food flavours, where the concentration of the flavouring ingredients appears in some cases to be at a similar low level.

Secondly, if the contaminant which it is thought might act as oxidation initiator is an organic material, then the point arises whether the carrier oil for the soluble catalysts, which have been used in so many of the tests under consideration to-day, may not have an effect on the test result, although I think that the evidence so far available is against this. Thirdly, if, in Dr Salomon's view, a " pure " oil does not easily oxidize, how does he reconcile this with the fact that highly refined oils are generally prone to oxidation?

Finally, I would like to make a comment arising out of Mr Bennett's paper. He has, among other tests, dealt with the measurement of power factor. It may be worth mentioning to those in the oil industry who may not normally be concerned with insulating oils, that power factor measurement can frequently be a convenient and delicate quality control test for oils that may have no electrical applications, such as white oils.

P. W. L. Gossling: As I bring the meeting towards its closure, I would like to be allowed to remind you that much of the work leading to the 1951 revision of the transformer oil specification was essentially completed in 1939, although it was not reported until the 1946 symposium. In other words, we are still reaping the benefit of the work which was carried out under Dr Michie as Chairman of the relevant ERA Committee. Many of you may know that Dr Michie only retired from his own active work in his consulting practice early this year, and I feel sure that you will agree that it would be appropriate for this symposium to record our good wishes to him for many years enjoyment of his retirement.

Comparing the papers and discussion at the 1946 meeting with those now presented, it is clear that interest has largely in the interim period turned away from a consideration of operational difficulties with transformer oils. Significant in this regard is that statement in the second paragraph of the Massey and Wilson paper. Current thought is upon the various possibilities of so improving these materials that they can be subjected to the more arduous conditions which designers of equipment may wish to impose in their search for higher efficiencies.

To this end the importance is clear of the improvement of methods for the assessment of oxidation stability with regard to the separate aspects of accuracy (in the prediction of probable results in service) and precision. It is seen that throughout the British collaborative work for IEC there has been an emphasis upon precision at each step, and it appears that the high standard essential for a test to replace IP 56 has not yet been demonstrated. Accuracy is of equal importance, and it has to be admitted that the method in BS 148 is probably effective in this regard only to the extent of defining the approximate limits of a band of oils which are dependable. It is natural, therefore, for the reasons given in the paper upon the ERA/IEC work, that the possible use of soluble instead of metallic catalyst should have aroused such interest. Massey has mentioned as a possibility the choice of metallic copper-resistant oils for new transformers containing no varnished coils and of oil especially resistant to soluble catalyst for new transformers containing varnish-impregnated coils, or for old transformers containing acid oil in the windings. However, Thompson has now shown, by the comparison of results obtained with " corresponding test conditions," that a high degree of correlation exists between the test results with a metallic copper catalyst on the one hand, and with a soluble catalyst on the other.

It has been stated in the second paper of this series that ERA has discontinued direct work for IEC in the development of a new testing method, concentrating its work in the meantime upon more fundamental studies, as have been reported in papers at this meeting. The time may soon be ripe for a resumption, and in the planning of this work, as of further fundamental studies, the wider discussion that is to be expected at the present symposium will be invaluable.

The last symposium was under the chairmanship of E. A. Evans, who is here tonight and has kindly offered to move a vote of thanks to those who have written papers and to the speakers in the discussion.

E. A. Evans: I suppose that I have been given the privilege of proposing the vote of thanks, because I have been associated with insulating oils for a period probably longer than anyone else in this theatre. In the audience I see Professor Weiss, who must be regarded as one of the pioneers in this field.

My first association with insulating oils was with Dr Michie in the Wallsend laboratories in 1914, when the sludge test was in its cradle, and when mineral transformer oils were on trial, which is slightly different from saying that they were a trial, but they were.

Throughout the forty-four years which have now passed, an unravelling of problems has been occurring at a slow, but gradually accelerating pace, not always without obstructions and prejudices. Consider for one brief moment the suggested use of antioxidants, which I made many years ago, and the violent opposition it received.

Now they are accepted and proclaimed, even if they have not caught on as Dr Forrest suggested. Low sludge value oils were kept alive until 1939, when the difficulties of war inflicted a change of face.

When the war terminated, a momentous meeting was held in this theatre in 1946 to evaluate the state of our knowledge and practice, both in the academic and applied fields. A revision and refocusing of personal contacts and ideas followed. National barriers disappeared, fundamental research at universities was harnessed, and disparity gave way to unison. The march of time and science has gone on with ever encouraging success.

Now I wish to propose a vote of thanks to all who have rendered special service to the improvement of insulating oils in this country and overseas.

We must not forget the pioneers, or those authors of papers who have contributed to this very successful symposium. Now let us give thanks to the organizers under the chairmanship of that modest and diligent worker, Mr Gossling. We owe a great debt of gratitude to the Council of the IP, under whose ægis we meet to-day, and to the IEE for their hospitality.

CONTRIBUTED DISCUSSION

K. H. Stark: Mr Bennett has mentioned the work being done by CIGRE on the influence of the test-cell construction on the measured loss angle of an insulating oil. This point was investigated by the ERA six years ago * as a result of the conflicting results obtained by CIGRE.

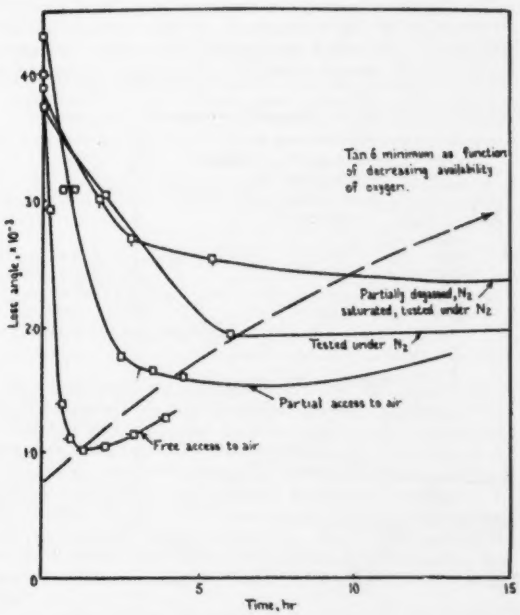

FIG E

VARIATION OF LOSS ANGLE OF THE OIL WITH TIME WHEN MAINTAINED AT 109° C WITH VARYING ACCESS TO OXYGEN

Four test cells were compared, the NPL cell, the Bramley cell (both illustrated in Mr Bennett's paper), the Berberich cell, and a modification of this cell by BTH. It was found that over the temperature range from 20° to 70° C the loss angle of the oil measured in the simpler cells was repeatable on different transformer oil samples. The maximum difference occurred at the highest temperature, and was 3×10^{-4} or 0·0003 at 50 c/s. The more complicated cells, on the other hand, sometimes exhibited sudden and permanent increases in the loss angle. It was concluded that all electrical insulation in a cell should be limited to quartz and that a guard-electrode, which is unnecessary with quartz, should not be used, as this simplifies the construction of the cell, allowing easier handling and more effective cleaning. The method used for cleaning the test cells has been accepted and approved by CIGRE.

At temperatures above 70° C, consistent results between the different cells may not be obtained. This is due to the loss angle of the transformer oil changing during the time required by the larger test cells to achieve thermal equilibrium, as is shown in the diagram (Fig E). The loss angle above 100° C can fall to a quarter of its initial value. This fall is caused by oxidation of the oil, and as the amounts of oxygen available to the oil are reduced the change in the loss angle is decreased.

C. Ericson: At this symposium three out of nine papers discussed oils containing additives. This fact must signify the increasing interest in these types of insulating oils. Nevertheless, on the consumer's side there still exists some hesitation in using such oils in transformers. In my opinion this hesitation stems from the lack of standardized test methods of good repute similar to those used for uninhibited oils.

Two of the authors of papers concerning oils with additives have carried out their experiments applying the oxygen absorption technique. These methods, however, although handy and informative to oil chemists, may be difficult to put into practice outside this circle. From the consumer's point of view I think it would have been appreciated if the authors had made even greater attempts to associate their very interesting and comprehensive work with some well-known, conventional test methods.

To do so is possible, as has been demonstrated by R. Irving and D. W. Bravey † in a paper on tests on inhibited oils using the IEC test method.

* ERA Reports E/T 60 and 61.

† ASTM Special Technical Publication No. 172 (1956), pp. 48–56.

The IEC apparatus is easy to handle and is simple and inexpensive. The results are obtained as figures for sludge and acidity, which are familiar to everyone who is dealing with transformers. Originally the IEC method

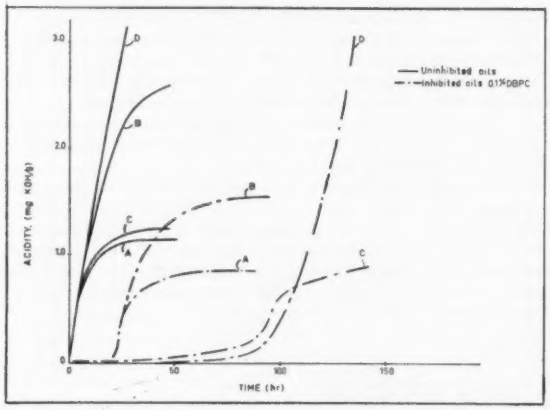

FIG F

OXIDATION OF FOUR OILS WITH AND WITHOUT AN ADDITION OF 0·10% DIBUTYL-*P*-CRESOL

Catalysts: 20 p.p.m. Cu + 20 p.p.m. Fe, 100° C. IEC conditions apply otherwise

was developed for testing uninhibited oils. In their paper Irving and Bravey confirmed our view that the method could be applied to inhibited oils as well. Moreover, the results obtained could be closely correlated to those of the static oxygen absorption method. This important extension of the use of the IEC method facilitates comparisons both between uninhibited and inhibited oils among themselves and also between laboratory results of accelerated tests and performance results of the oil in service, all the time using the same well-known indices of aging, namely, sludge and acid formation.

As an illustration of the use and applicability of the Irving–Bravey extension of the IEC method some results of a few, though not systematic, test series can be mentioned.*

A series of tests was carried out with the intention of studying the soluble catalyst test technique of Irving and Bravey. Some oils of various origins, all uninhibited, were oxidized in accordance with the IEC method. After addition of the well-known inhibitor dibutyl-*p*-cresol to other samples of the oils these, too, were tested under the same conditions. The results of the acidity determinations are shown graphically in Fig F.

The two oils A and C fulfilled Swedish requirements for normal transformer oils. Oil B was a little more severely treated, and oil D was an over-refined white oil. The duration of the oxidation of the inhibited oils was extended a good way past the induction period.

The curves of the uninhibited oils are typical. The normal treatment of the oils A and C is reflected in almost identical curves, indicating the moderate increase of acidity. Oil B, being on the borderline to overtreatment, produced a somewhat higher acidity. The white oil D was clearly distinguished by a very rapid formation of acids.

The inhibited oils had various induction periods. However, after the termination of these periods the inhibited oils performed similarly to the uninhibited ones, giving curves almost identical with those of the latter

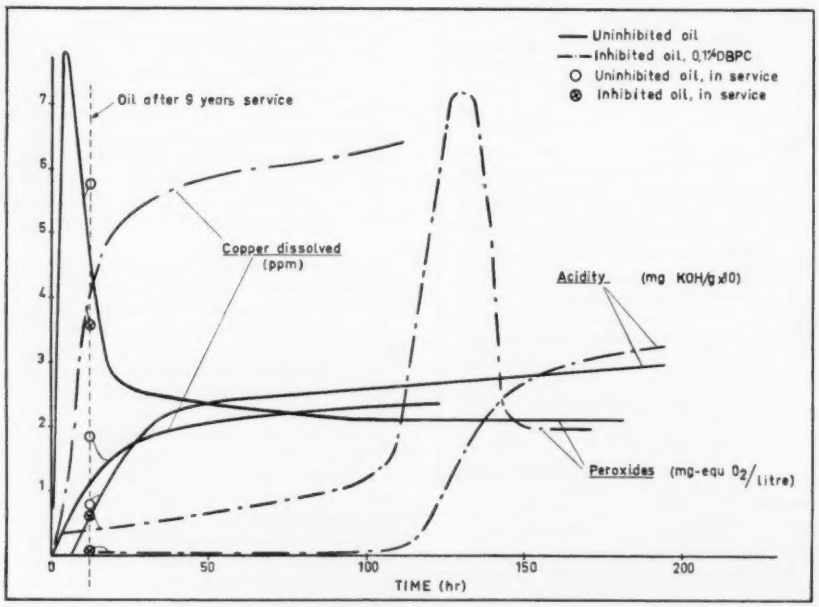

FIG G

OXIDATION OF A SWEDISH TRANSFORMER OIL WITH AND WITHOUT AN ADDITION OF 0·10% DIBUTYL-*P*-CRESOL

Two copper spirals (23 cm²), 100° C. IEC conditions apply otherwise

* *ASEA Jl*, 1958, **31** (1–2), 16–21.

but displaced along the time axis, so that they were parallel.

If these results can be generalized, the consequence will be that an oil consumer is able to control the base oil without paying any regard to the inhibitor. Also, he can use the method for controlling the inhibitor concentration for effectiveness from the length of the induction period.

Some hints on correlating laboratory test results and results from oils in service can be gained from another series of tests.

An oil fulfilling the Swedish requirements was oxidized in accordance with the IEC method, using solid copper catalysts. Another sample of the oil was doped with dibutyl-*p*-cresol and oxidized in exactly the same way. After varying times the oils were examined with regard to acidity, amounts of copper dissolved, and peroxides, the last determinations being carried out in accordance with a method published by M. Zurcher and J. Luder.* Fig G shows the test results.

The curves for acidity and peroxides are identical for both of the oils, although those for the inhibited oil are moved along the time axis, so that again they were parallel.

Copper dissolution, on the other hand, seems to take place independently of the induction period. The amount of copper dissolved in the inhibited oil is about twice as much as that in the uninhibited oil.

In the graph these results are compared with some observations on oils from two similar transformers working in parallel in normal service. After nine years' use the oils were analysed, with results reproduced in the table below.

TABLE A

Results of an Investigation Carried Out on Inhibited and Uninhibited Oil after Nine years' Service in Two Similar Transformers Working in Parallel

	Without inhibitor	With inhibitor
Colour	Yellow	Pale yellow-yellow
Saponification No., mg KOH/g	0·37	0·17
Acidity, mg KOH/g . .	0·08	0·04
Copper content, p.p.m. . .	0·19	0·36
Iron content, p.p.m. . .	0·23	0·30
Peroxides, mg-equiv. O_2/litre .	5·8	0·7

The inhibited oil was produced by the addition of dibutyl-*p*-cresol to the uninhibited one, unfortunately not of the same quality as was used in the laboratory tests reported above. Nevertheless, the conditions of both oils in service correspond closely to those reached after about 12 hours accelerated laboratory oxidation of the oils with regard to acidity, as well as to concentration of peroxides and copper dissolved. For comparison the results shown in the table are indicated in the graph by the vertical dotted line at the 12 hours point of the time axis.

I am quite aware of the limitations of the test series just mentioned. However, it seems to me that the method used displays some possibilities which may be worthwhile exploring in some future investigation.

C. G. Garton: I should like to support Mr Reynolds' view that the life of oil-impregnated paper insulation depends upon several factors other than, and often more important than, the inherent properties of the oil used. As Mr Reynolds remarks, the " gas absorption " of oils has been investigated for many years, without producing any unequivocal result. It is a fair assumption, in such a situation, that other factors in the problem are being overlooked. There are indeed several such factors, but the small group which has been working for some years on the subject at the ERA is now able to isolate and identify a few of the processes involved. I propose to analyse the problem into some of its constituent parts.

Failure of liquid-impregnated paper insulation occurs through at least three distinct processes:

(1) Thermal instability, which is well understood and needs no further comment.

(2) Electrochemical attack upon the cellulose, due to ions dissociated from dissolved impurities and transported electrolytically to the electrodes, where they enter into chemical reactions which may or may not be destructive, depending upon the nature of the ions. There is no stress limit below which this process is inoperative; it is, of course, accelerated by increase of stress, but more strongly so by increase of temperature. It does not normally lead to liberation of gas. It may terminate the life of insulation after a considerable period of apparently satisfactory operation, especially if the impurity must diffuse from some external source (case linings, terminal washers, sealing gaskets, etc.) before reaching highly stressed insulation. Such impurities can be detected, extracted, and examined by suitable techniques.† They may occasionally be present in the oil itself, when they are revealed by increased conductivity of the oil, especially at high temperatures. Failures of this type have been thoroughly investigated,‡ and the findings confirmed by some years' further experience of post-mortem examinations. They are commoner than is generally recognized, and are not limited to the case of d.c. stress.

(3) Liberation of gas within the dielectric involves a number of processes, which require consideration separately:

(*a*) Oil in contact with free gas, as in a partially filled tank, must dissolve gas until it is in equilibrium with the ambient pressure. If the latter is then reduced, as by a change of temperature or otherwise, the oil is supersaturated with respect to the new pressure, and will liberate gas bubbles either spontaneously, if the reduction of pressure is sufficient, or under relatively low electric stress. This gas has not been chemically derived from the oil, but merely thrown out of the solution. The role of stress in facilitating its liberation in this non-chemical case is not yet known.

(*b*) Application of electric stress to an oil which is in (or below) equilibrium as regards its gas content, and which is entirely free from solid particles, does not liberate gas at any stress below the breakdown strength of the oil.§ Statements in the literature to the contrary are due either to supersaturation as under (*a*) or to the presence of microscopic solid particles which act as under (*c*). It is to be understood that the stress is applied only to the oil, and not to include gas bubbles, nor to any gas space above the oil. Ordinary gaseous discharges in such spaces would, of course, invalidate the argument.

(*c*) Oil with a dissolved gas content in (or below) equilibrium will generate gas upon application of a sufficient field only if there is present a solid phase, as particles,

* *SEV Bull.*, 1950, **41**, 511.

† Church, H. F. ERA Report L/T 375.

‡ Church, H. F. *Proc. Instn Elect. Engrs*, 1951, **98**, Part III, 113.

§ Krasucki, Z. ERA Report L/T 376.

or, more extensively, of some hygroscopic substance containing moisture.* It is again to be understood that no gas is initially present in the stressed region. The (a.c.) stress required to liberate gas by this process depends upon the moisture content of the solid, and can be varied between 10 and 120 V/micron (peak) by controlling the moisture content. Gas is liberated only at interfaces between the electrodes and the hygroscopic solid, or between two particles of the solid. It appears to be derived not from the oil, but from dissociation of the water into H_2 or O_2, since the effect occurs equally in a liquid which has no gaseous component, such as CS_2. The mechanism of disruption of the water is still obscure. There is some evidence that dissolved impurities in the liquid can be similarly disrupted at an interface.

(*d*) If the stress is applied to a gas-filled space above the oil, as in conventional " gassing " tests, or if a bubble exists initially in the oil, or if one is formed there by either of processes (*a*) or (*c*), the gas will be occupied, if the stress is sufficient, by an ordinary gaseous discharge.† The bombardment of the oil by this discharge liberates hydrogen from the oil molecule as a merely secondary process, and it is this alone which is much influenced by the gas-absorbing power of the oil as measured by the Pirelli and similar tests. Confusion of this secondary process with the primary one under (*c*) is the origin of much of the uncertainty which surrounds the subject. In some types of insulation, however, such as mass impregnated cables, it is normal for voids to be initially present. In this case, process (*d*) may be regarded as primary, and gas-absorbing power may be more important.

(*e*) At the degree of dryness normally achieved, and at normal working stresses in completely impregnated insulation, process (*c*) is inoperative,‡§ but it comes into action during switching surges, which occur at times upon practically all circuits. During such a surge, a bubble is generated by either process (*a*) or (*c*), and process (*d*) then supervenes. A discharge thus initiated in oil-impregnated paper is not afterwards extinguished unless the stress falls to about one-third of the initiating stress. If the working stress exceeds this value, the discharge persists after the surge, and deterioration will be rapid. If, however, the conditions are such that persistence of the discharge is marginal, the gas absorption properties of the oil may determine its persistence or extinction. It may be remarked in passing that extinction occurs much more readily in chlordiphenyl-impregnated than in oil-impregnated paper.

(*f*) It should now be clear that gas which appears in oil-impregnated insulation which was initially free of voids may have three distinct origins. It may be merely previously dissolved gas which has been thrown out of solution; it may be the product of disruption of moisture held in the paper; and finally, it may have originated from disruption of oil molecules by a gaseous discharge within voids created by either of the other two processes. Only this last and secondary stage involves the chemical nature of the oil.

(*g*) Initial dryness of the paper is not necessarily maintained during life, even with hermetic enclosure. Water is liberated by pyrolysis of the cellulose and by electrolytic reactions. Similarly, an initially correct gas pressure within an hermetic enclosure is not necessarily maintained. Gas may be dissolved in the oil, if this was not initially in equilibrium; oxygen may combine with the oil; and finally, every reduction of temperature is accompanied by a transient reduction of pressure due to thermal contraction. For all these reasons the discharge inception stress may fall during life.

(*h*) The foregoing indicates that " gas absorption " plays only a limited and secondary role in determining the life of completely impregnated insulation. Further, results of life tests may be unintelligible, and largely meaningless, unless the following factors are controlled:

Pressure on the liquid throughout the test period.
Moisture content of the cellulose.
Purity of all components in the system, including those remote from the actual insulation and possibly intended to play only a mechanical role.
Presence or absence of discharge inception at the maximum surge voltage occurring on the test circuit.

It is by no means easy to conduct tests which comply with these requirements, but those which do not are of little value and tend to increase the existing confusion of thought on the subject.

C. N. Thompson: In reply to Mr Tobin, we have looked at this aspect pretty thoroughly. In my paper there is evidence in the text relating to Figs 8 and 9, showing that high concentrations of soluble catalysts are undesirable, since they lead to misleading results.

Dr L. G. Wood has drawn some interesting comparisons between the results reported in his paper and in mine. These help to prevent anomalies being seen where there are in fact none. It is evident, as pointed out by Dr Wood, that the experimental conditions in the two investigations were substantially different. Similar factors may be the cause of the discrepancy between Dr Wood's " useful life period " of 1000 ml, and Mr Massey's of 300 ml. Perhaps it is coincidental, but in one of our earlier papers from Thornton Research Centre (*J. Inst. Petrol.*, 1951, **37**, 30) we quoted a mean figure of 650 ml/oxygen per 100 g oil as corresponding to an acidity development of 1 mg KOH/g or the useful service life of an oil. It so happens that this is the arithmetic average of the figures now proposed in 1958 by Wood and by Massey!

A number of speakers have talked about inhibited oils. Although in my opening remarks I said I would try to refrain from touching upon this question I would like to reinforce Mr Ericson's view that the Irving/Bravey version of the IEC test deserves more attention than it has received. It involves a simple extension of the test now coming into almost universal use throughout Europe for testing uninhibited oils. As such, it is a valuable addition to the insulating oil test facilities of those laboratories which have not yet equipped themselves with a static oxygen absorption apparatus for examining the potentialities and service performance of inhibited products.

G. E. Bennett: I agree with Mr Stannett that d.c. resistivity tests are, in practice, as informative as dielectric loss angle (power factor) tests when one is investigating the characteristics of hydrocarbon mineral oils, and also rosin-compounded cable saturants at elevated temperatures. However, if one is investigating the subject from a general point of view it is as well, I think, to bear in mind that D.L.A. measurements may be more informative than d.c. tests. Considerable per-

* Krasucki, Z. ERA Report L/T 376.
† Mason, J. H. *Proc. Instn Elect. Engrs*, 1953, **100**, Part IIA, 149.
‡ Church, H. F., and Garton, C. G. *Proc. Instn Elect. Engrs*, 1953, **100**, Part IIA, 111.
§ Cucha, P. ERA Report L/T 356.

centages of rosin (natural colophany), a polar material, are generally added to power cable saturants in Europe, and the effect of such addition on D.L.A. below about 40° C is very apparent. I agree that apparatus for the routine determination of D.L.A. is, in general, rather more expensive than that for d.c. resistivity measurements, but moderately-priced commercial equipment is available. A higher degree of skill is required of the operator of a bridge network to obtain the balance position, or null point, than is required for taking a d.c. reading, and this may, at times, be inconvenient for field testing.

Mr Biske has recalled an interesting point, that power factor measurement can frequently be used as a control test for oils that may have no electrical application. In this connexion it was found during the second world war that power factor measurement was a reliable guide to the demulsification properties of steam turbine oil, and much more convenient to carry out in a suitably equipped laboratory than the rather elaborate demulsification test specified at that time.

I am familiar with the two ERA reports to which Mr Stark refers. The question whether to proceed with a two-terminal test cell for D.L.A. measurement on an international basis or a three-terminal guarded cell was debated, at some length, at a CIGRE meeting two years ago; but it was the general opinion of the Oil Study Committee members and other experts present that a test cell to have international approval should be of a three-terminal design. Mr Stark refers to inconsistent results obtained on D.L.A. measurements of transformer oil at temperatures above 70° C. It must be remembered that transformer oil is not refined to a D.L.A. specification initially, nor are there any limits imposed on this characteristic after oxidation. In the experience of many laboratories, consistent results may be obtained with different test cells at temperatures above 70° C on cable insulating oils which have been refined with these requirements in view. Difficulties may be experienced when measuring the D.L.A. of poor quality oils, having a low resistance to oxidation, at high temperatures if the test cell used requires, on account of its large mass, a prolonged period of time to achieve thermal equilibrium.

OBITUARY

JOHN LAMB, O.B.E.

1889–1958

It has come as a shock, if not as a surprise, for John Lamb had been ailing for many years, to hear of his death on 12 August 1958. John Lamb was loved by many and, quite apart from his engineering successes, he did, by his very nature, endear himself to his associates in the oil industry. I was fortunate enough to be his proposer for the IP, and I have in many ways been associated with him, directly and indirectly, for many years. He began his life with the oil industry as Fourth Engineer on the *Oweenee*, a converted sailing ship which I was to know very well for ten years as the tanker which brought all the crude oil to the Anglo-Egyptian Oilfields refinery at Suez.

John Lamb soon found himself promoted and, through the usual channel of Marine Superintendent, he eventually arrived at the London office of The Anglo-Saxon Petroleum Company, where his interest in development gained him a firm place in the research and development side of the tanker fleet. I was fortunate enough to be associated with him in the decision to put the first tanker to sea equipped with a gas turbine, and to hold many discussions with him on this and other matters.

John Lamb obtained many honours in his life. He was twice awarded the Denny Gold Medal by the Institute of Marine Engineers, once for his work on the burning of heavy fuel oils in diesel engines and once for his paper on the marine gas turbine engine. He was given the Herbert–Akroyd–Stuart prize by the Institution of Mechanical Engineers for his work on the prevention of crankcase explosions, and was awarded the James Medal by the North-East Coast Institution of Engineers and Shipbuilders for his studies on the protection of tanker hulls from corrosion. In fact, his interests ranged widely from the development of fireproof wooden lifeboats to the conversion of tankers to merchant aircraft carriers, and for these works he was awarded the O.B.E. in 1947.

He will be greatly missed by those of us who have worked with him for years, for although one could disagree with Lamb on many points, one could never feel the slightest antagonism. Those who worked under him always looked upon him more as a friend than as a head of a department, and his kindly outlook on everything will be sadly missed by those of us who knew him intimately. We should also like to extend our sympathy to his bereaved wife and family.

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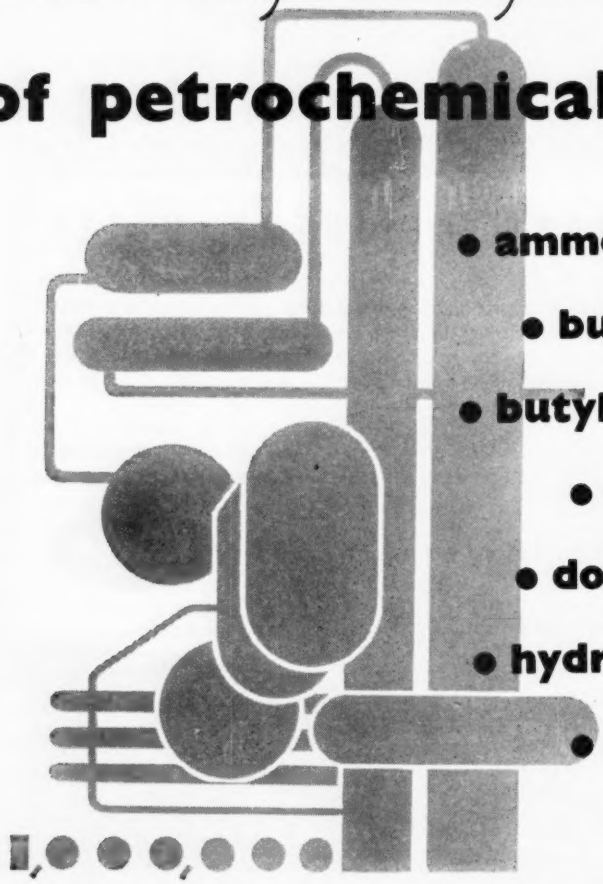

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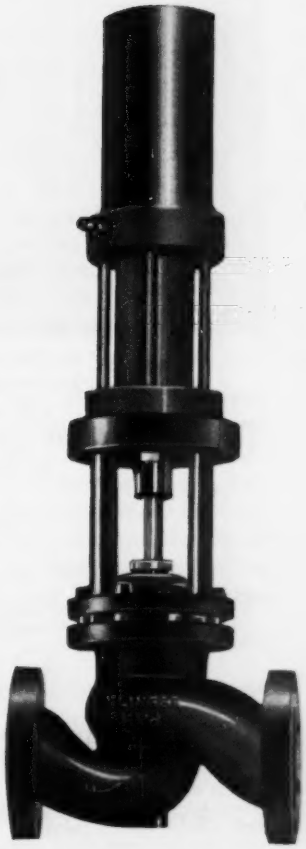

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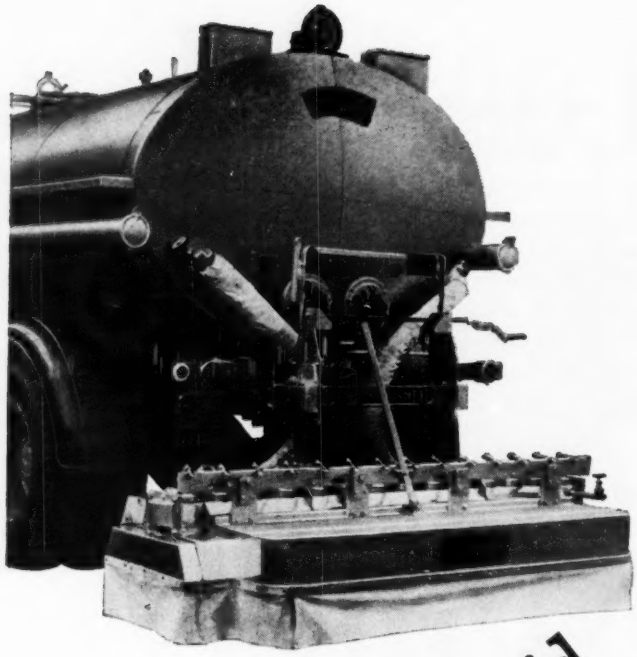
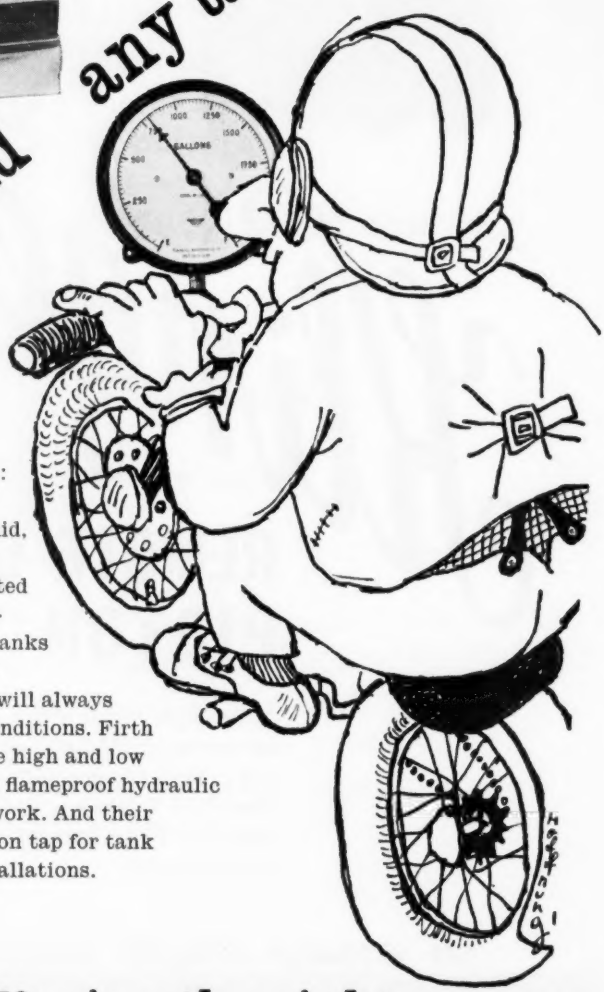


any liquid any tank anywhere



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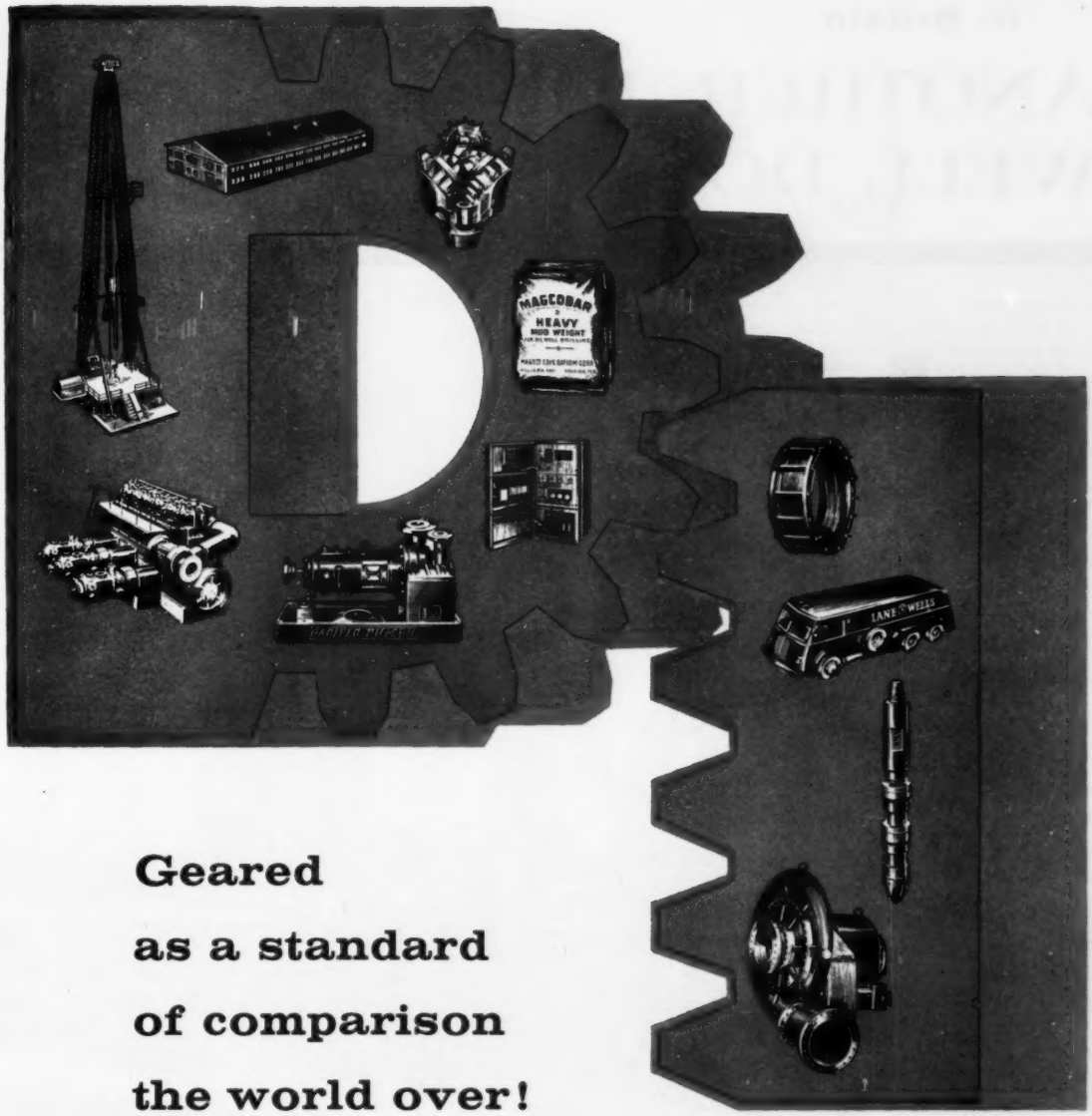

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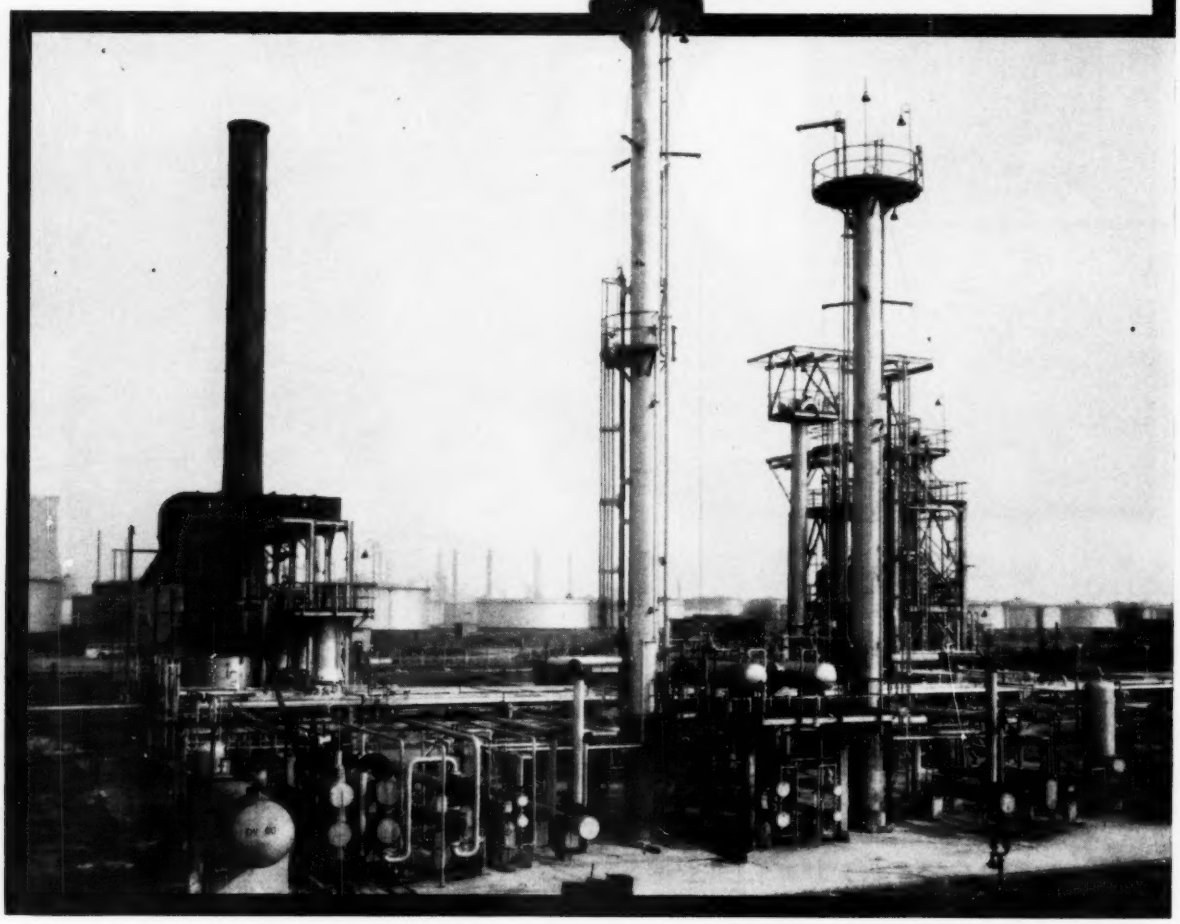

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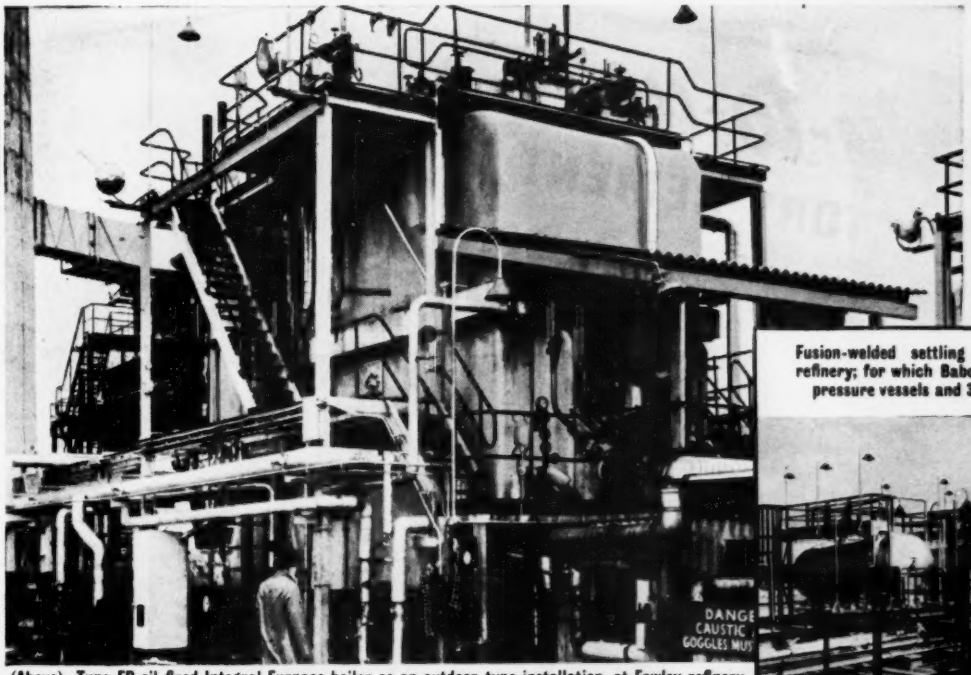
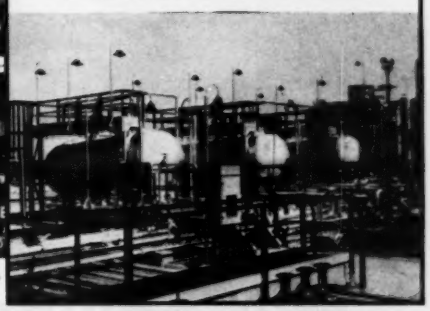


(Above) Type-FP oil-fired Integral Furnace boiler as an outdoor-type installation, at Fawley refinery.

Fusion-welded settling tanks, at Coryton refinery; for which Babcock supplied over 90 pressure vessels and 30 vertical columns.



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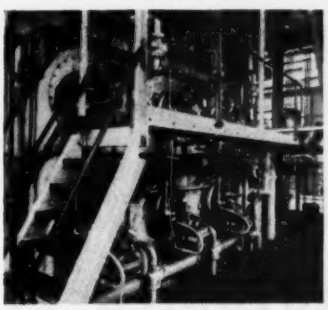
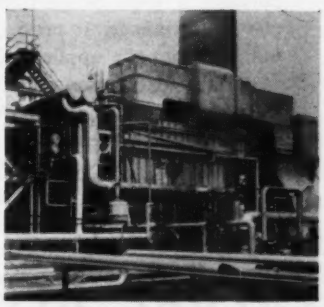
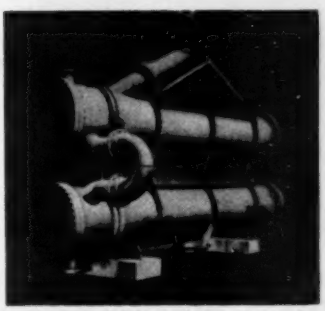


Oil-firing equipment on type FH boiler, Fawley refinery.



Type FH, oil-fired, Integral Furnace boiler as an outdoor installation.



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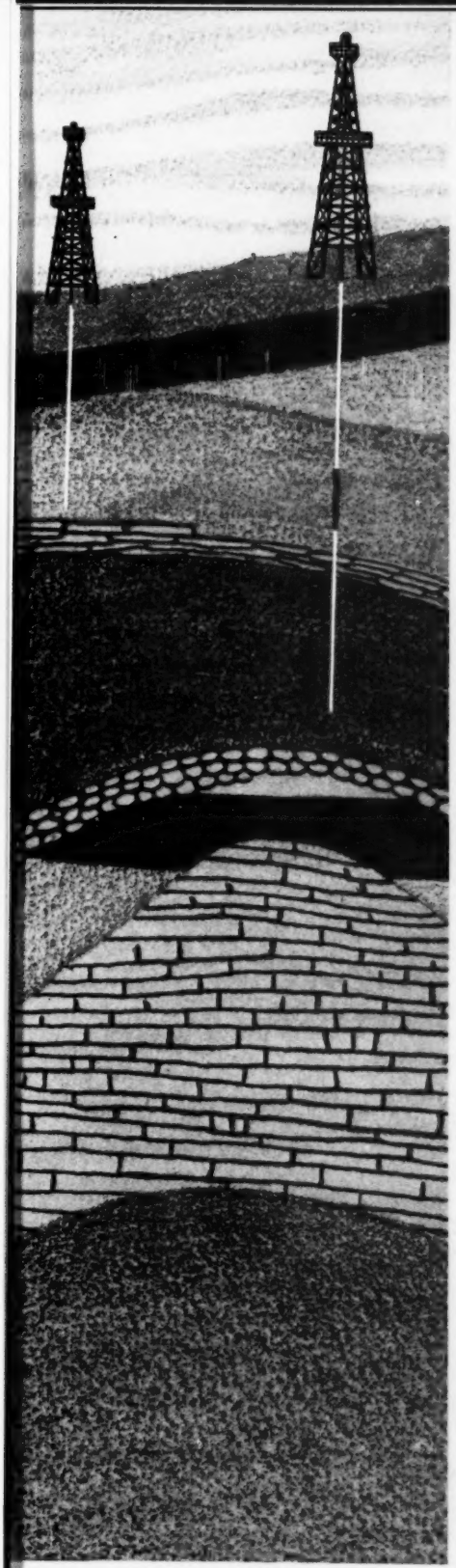

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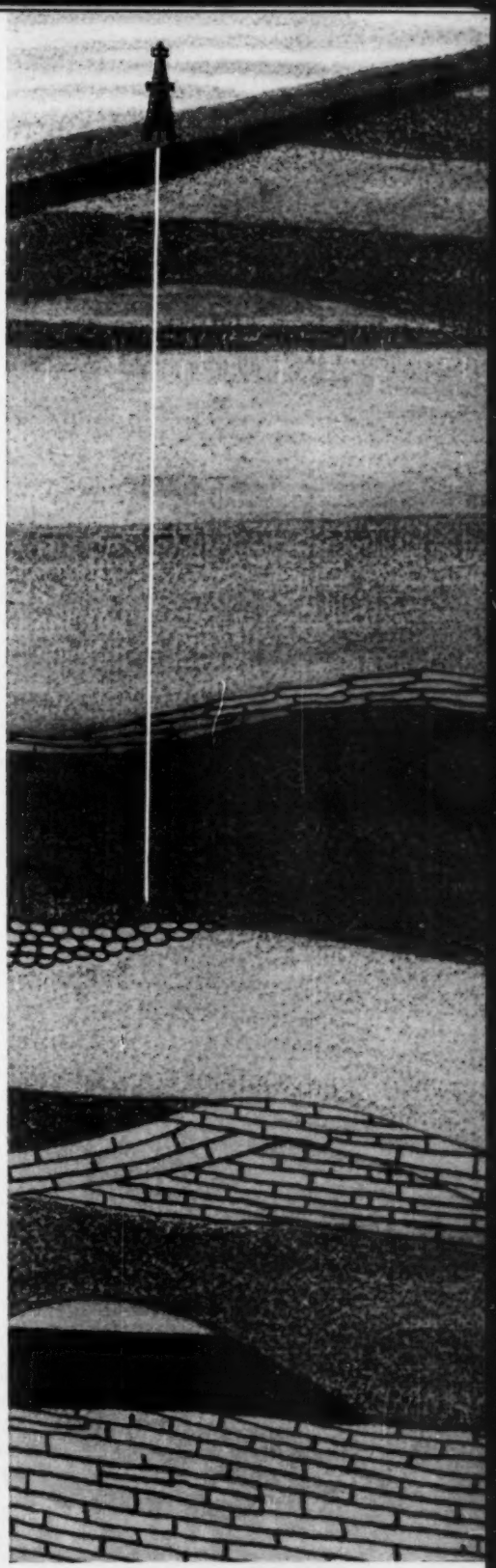

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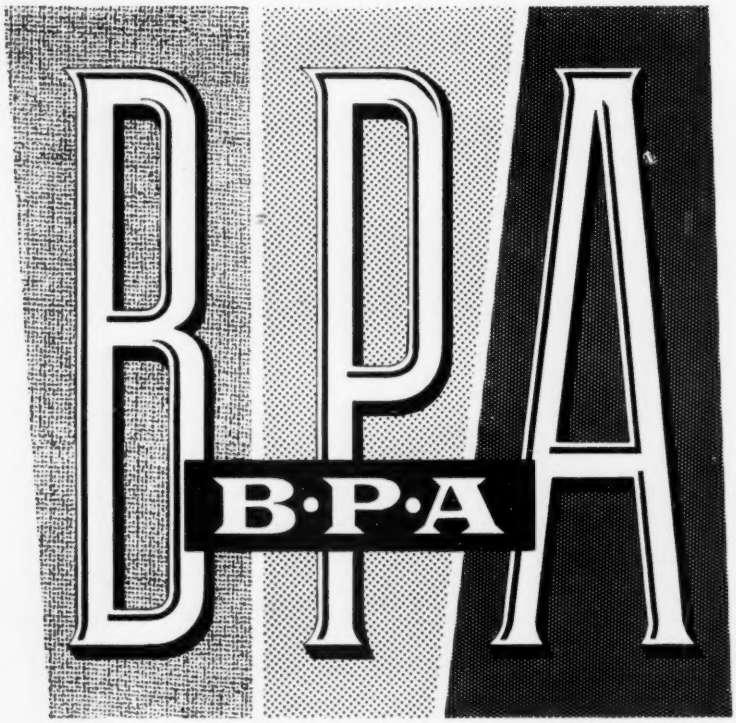

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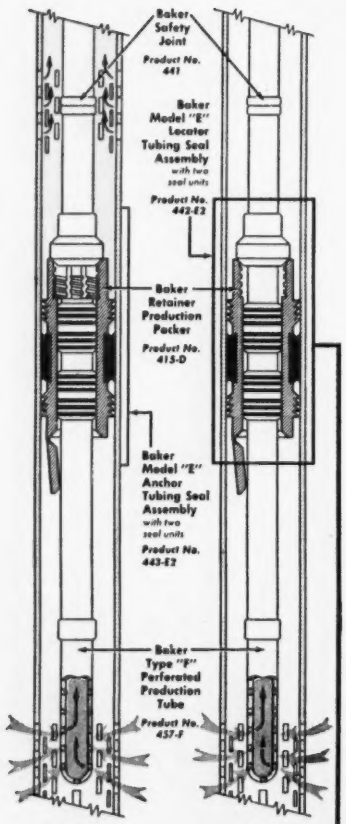
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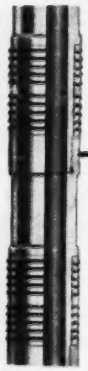

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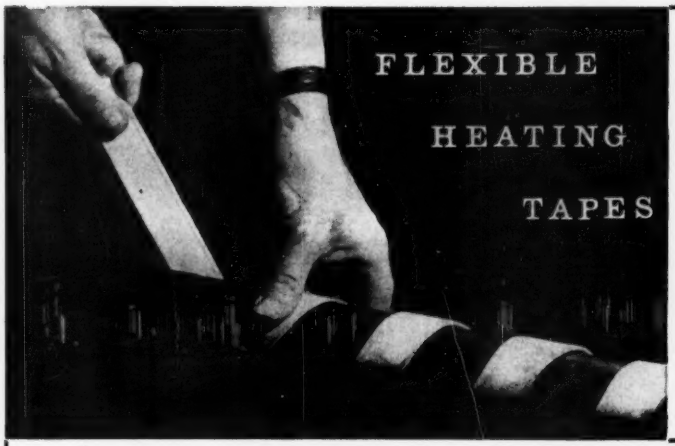

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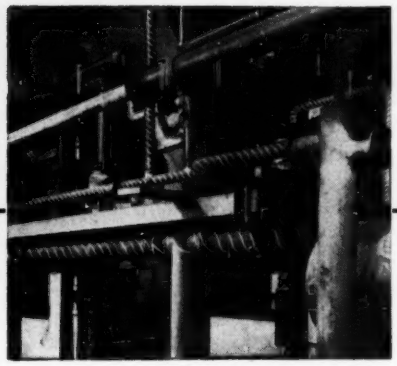

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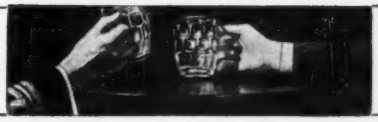
Let's sit down and talk about cricket, the weather... anything so long as it isn't your confounded Simmonds Fram Separators.

Sorry old man . . . didn't mean to bore you.



That's quite all right. Delighted to know the R.A.F. is getting up to date. So you actually fly your planes on kerosine now instead of water!

Very comical! Anyway, it's not the whole point. I admit the main object of Simmonds Fram Separators is to remove all the water, but they also take out the solids.

Little strips of erk, for instance?

. . . Anything down to 5 microns.

That gives me a big kick.
Which is more than I can say for this brew . . .

There you are. Now if we could persuade Sally to fit Simmonds Water Separators to the barrels . . .

the point of the argument... **FRAM SEPARATOR FILTERS** for clean water-free fuel

For more details of this and other Simmonds products for the aviation industry **SEND FOR LITERATURE** *to*

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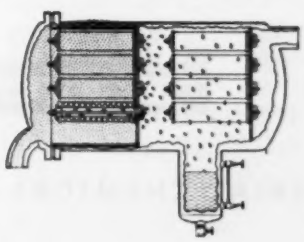

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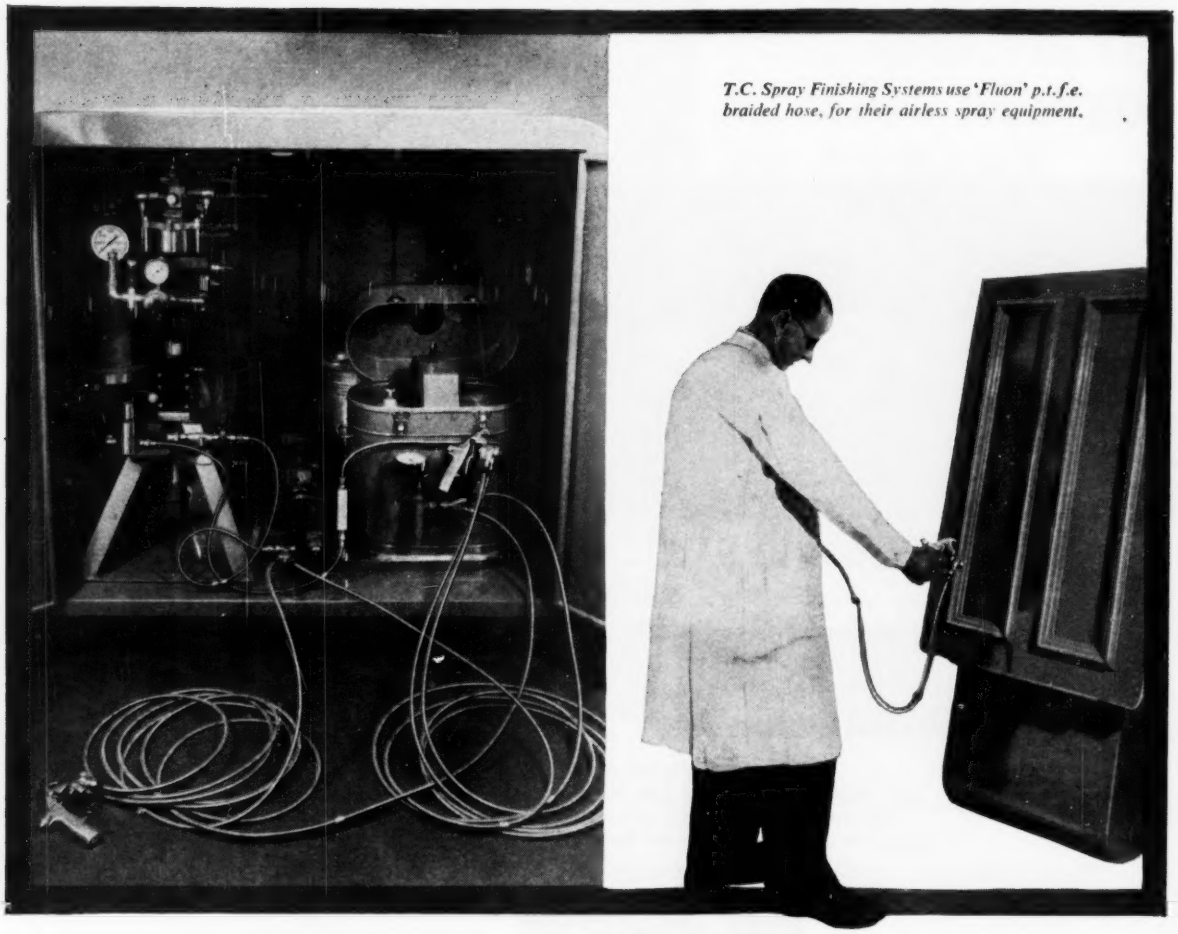
'FLUON' *increases production in the Petroleum Industry*



T.C. Spray Finishing Systems use 'Fluon' p.t.f.e. braided hose, for their airless spray equipment.

Complete resistance to solvents makes 'Fluon' first choice for paint spraying hose

'FLUON' P.T.F.E. is used for the braided hose made for T.C. Spray Finishing Systems. 'Fluon' was chosen because this outstanding material is the most inert of all plastics and resists every chemical except molten alkali metals and a few fluorine compounds. 'Fluon' tubing is flexible, as the illustration shows, and is most durable. Among its range of properties are its non-wetting characteristics and the temperature range within which it works (—80°C. to 250°C.)

'FLUON'

'Fluon' is the registered trade mark for the polytetrafluoroethylene manufactured by I.C.I.

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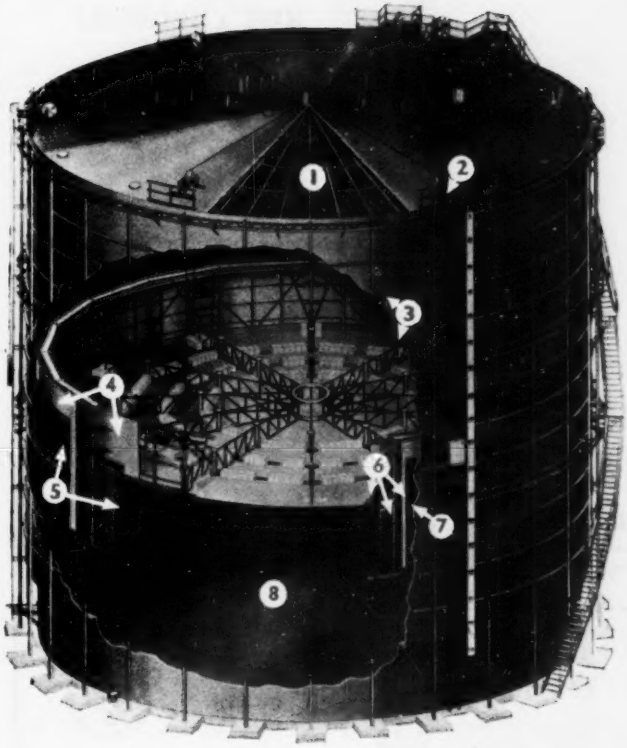
FEATURES OF THE *Wiggins*
DRY SEAL GASHOLDER



Wiggins Gasholders are being used for the storage of hydrogen, nitrogen, towns gas, carbon monoxide, carbon dioxide, oxygen, coke oven gas, tetrafluorethelyne and sewage digester gas, etc.

The Wiggins Gasholder operates on the principle of piston displacement. A frictionless, movable piston floats on the confined gas, rising and falling with changes in volume. The seal—a synthetic rubber-coated fabric—is protected against wear by ample clearances. The system requires practically no maintenance and no replacements. The Wiggins Gasholder is a structure free of unsightly framework.

Half full position, showing inflated seal constructed of a synthetic rubber-coated fabric.

Full position view of mechanically-operated relief valve. Releases gas if holder capacity is exceeded.

1. **The piston rises nearly to the roof of the gas-tight shell giving maximum capacity.**
2. **A single automatic levelling device keeps the piston riding level.**
3. **The section of the shell above the piston is completely ventilated.**
4. **Wide clearances prevent friction.**
5. **The gas-tight seal remains unaffected by weather.**
6. **Fenders protect the seal when under pressure and guide it on to the side walls without friction.**
7. **The shell is gas-tight up to the seal connection.**
8. **Foundations are simple and inexpensive as only the shell weight has to be supported.**

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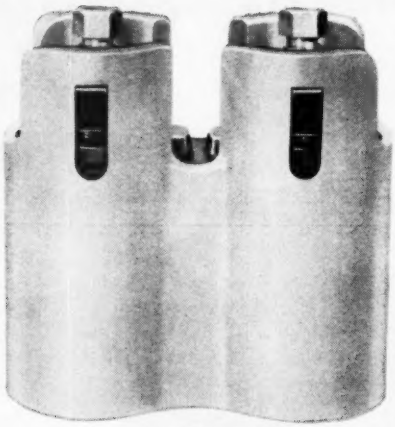

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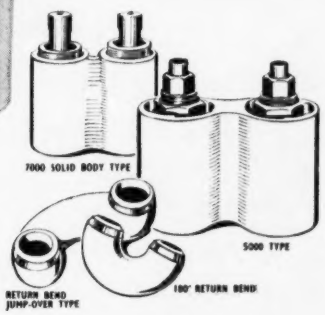

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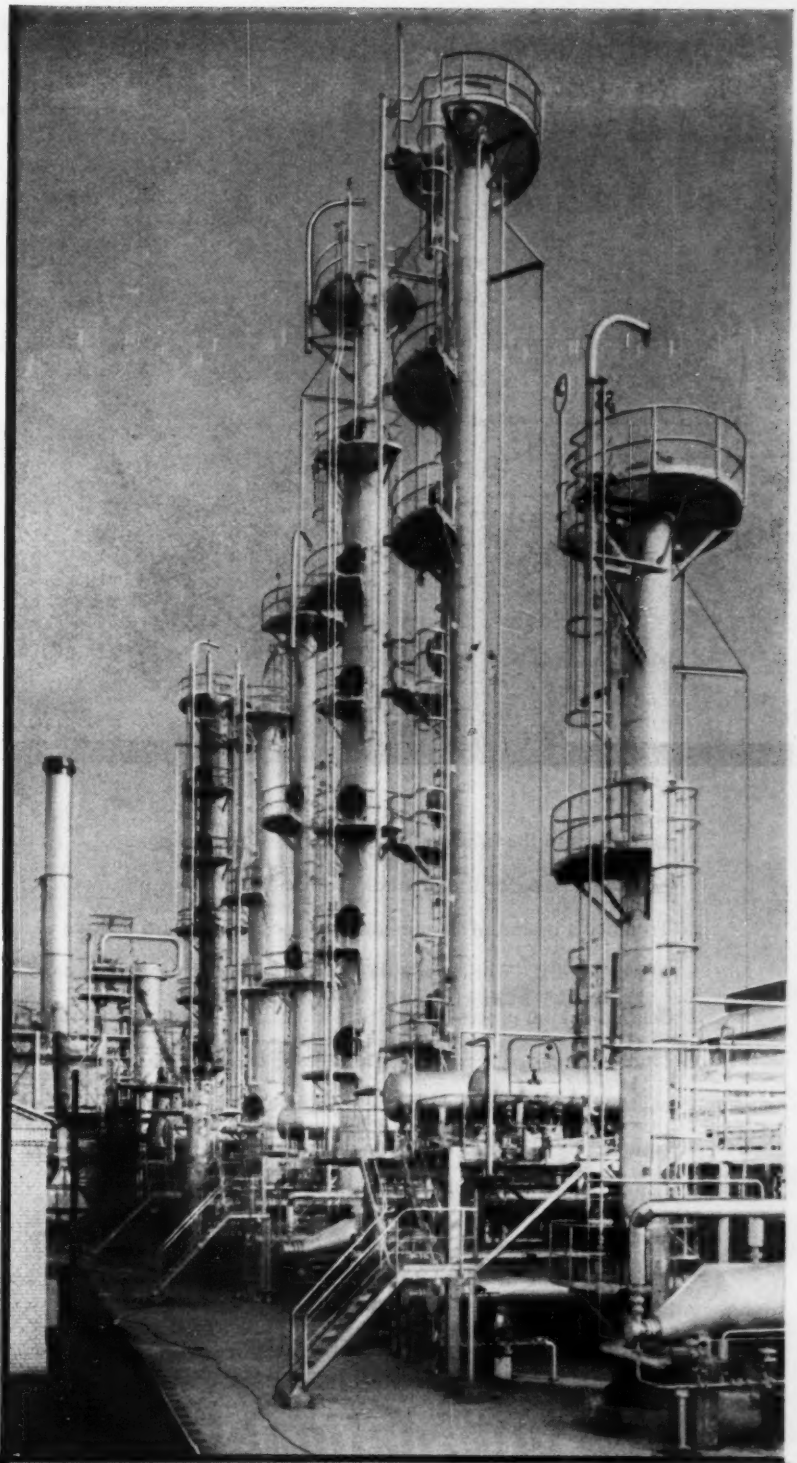
Platforming*

Unifining*

Processes



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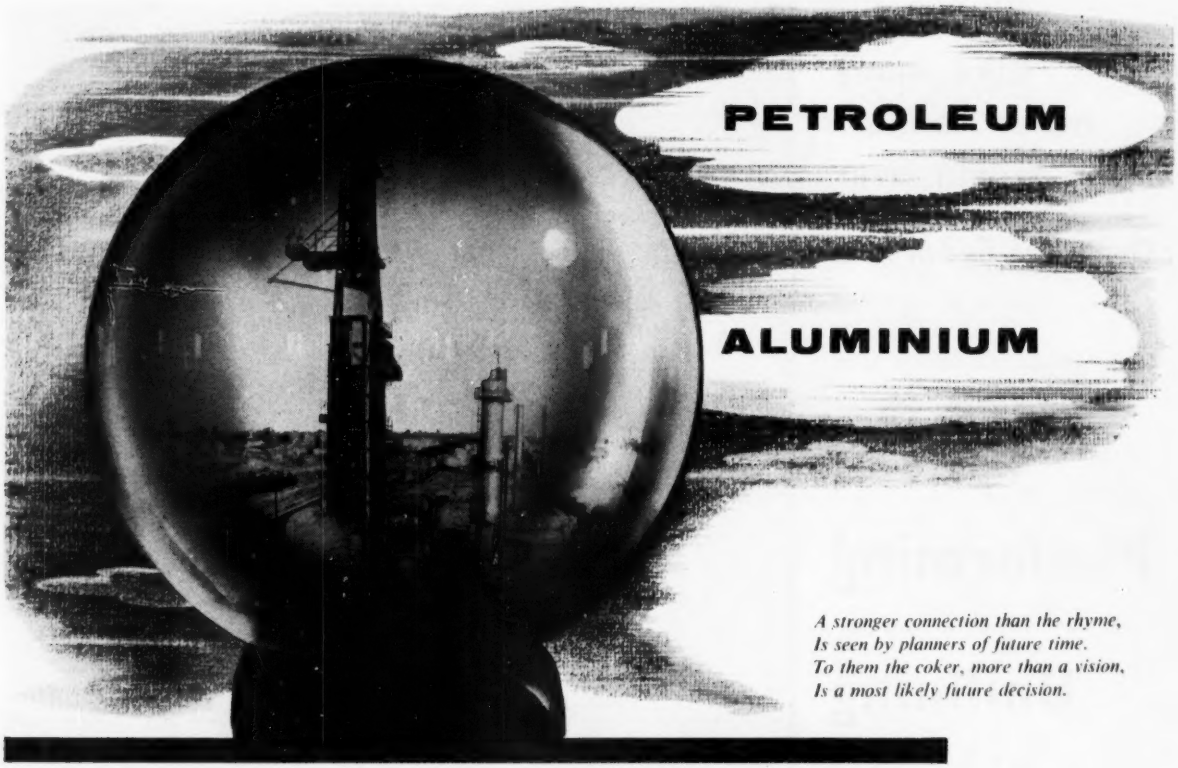
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Is a most likely future decision.

Looking into the future petroleum refiners can be expected to make petroleum coke for the expanding of British and European aluminium companies. To make a pound of aluminium requires half a pound of coke in the form of electrodes. Throughout the world the aluminium industry prefers to use coke made from petroleum by the delayed coking process rather than coke made from coal because of the latter's high ash eontent. During the last sixteen years the Kellogg organisation has on the average designed, engineered and constructed one delayed coking unit per year. The wealth of experience culminating from this continuing engineering programme to design and build better delayed coking units is available through the Kellogg International Corporation. Oil refining companies concerned with future planning are invited to discuss the economic and technical aspects of delayed coking or of any other refining process with the Kellogg International Corporation.

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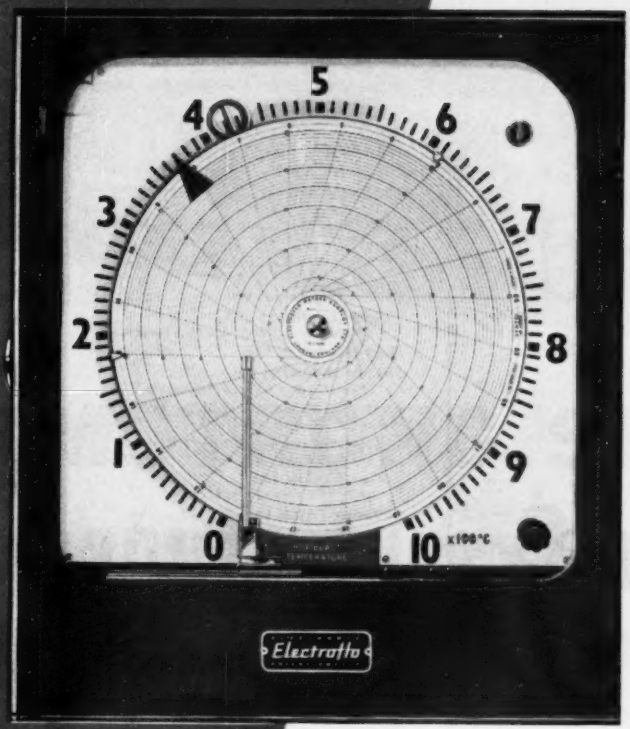

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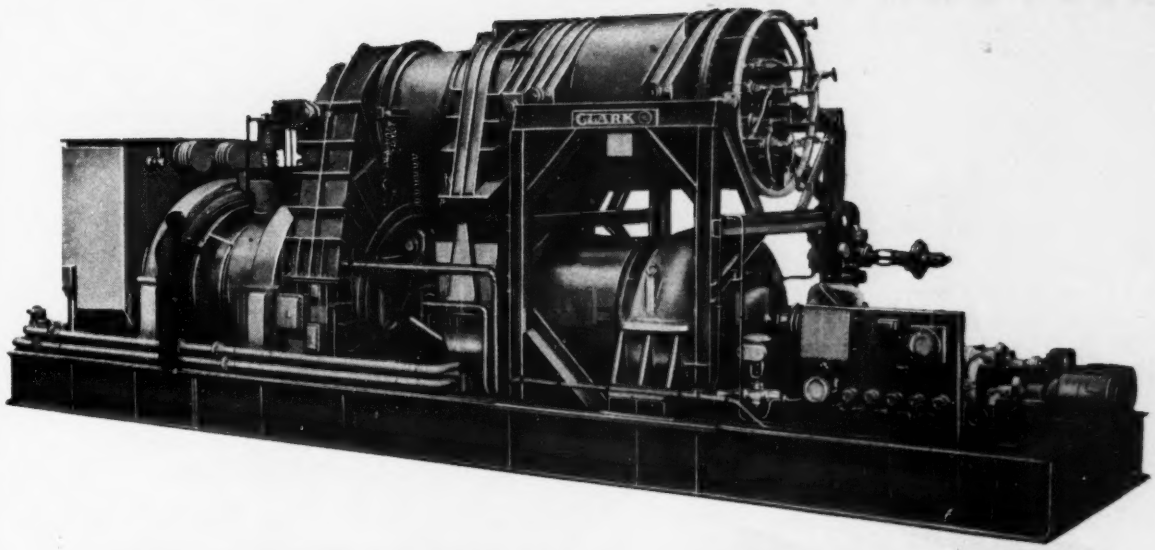

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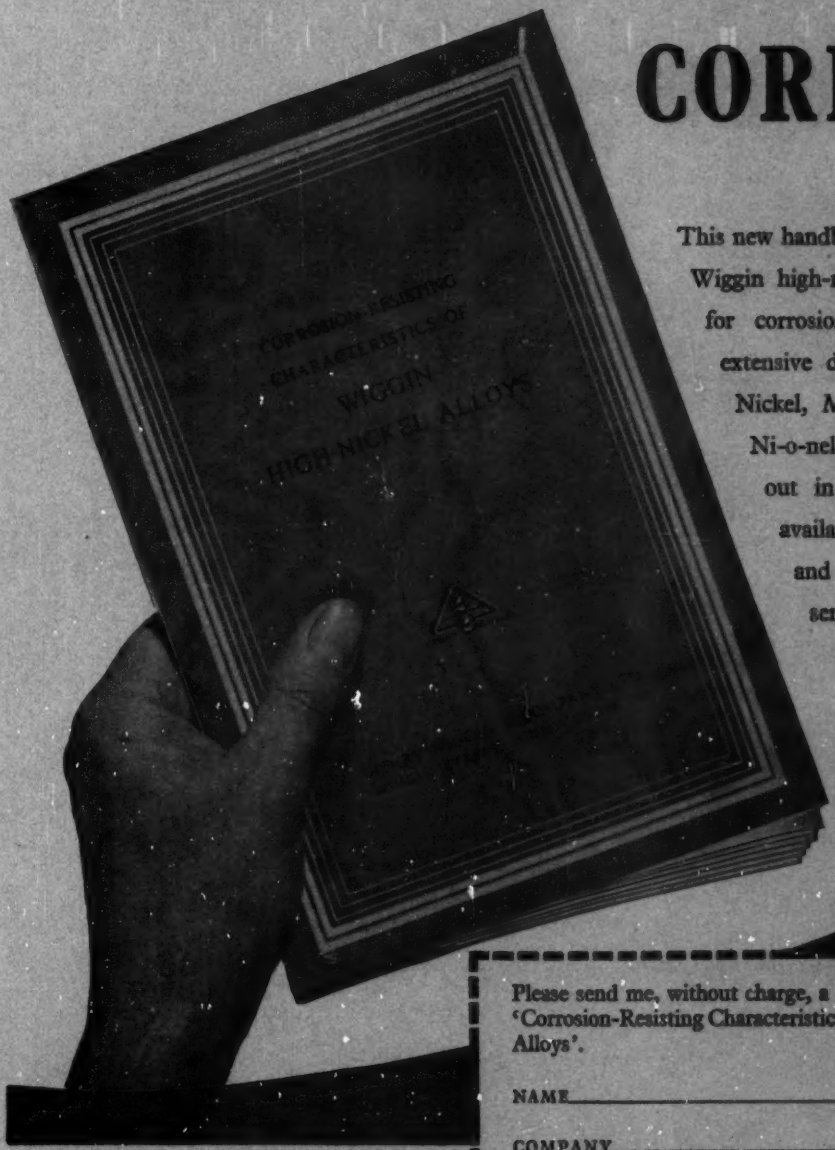

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